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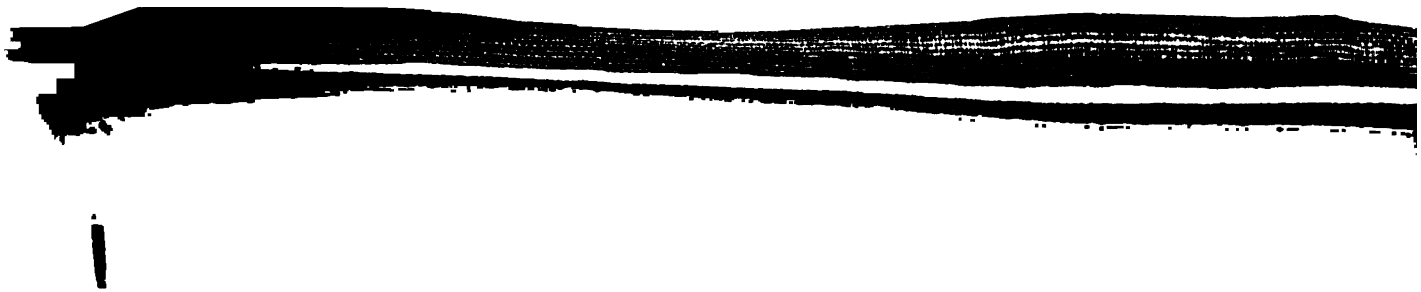

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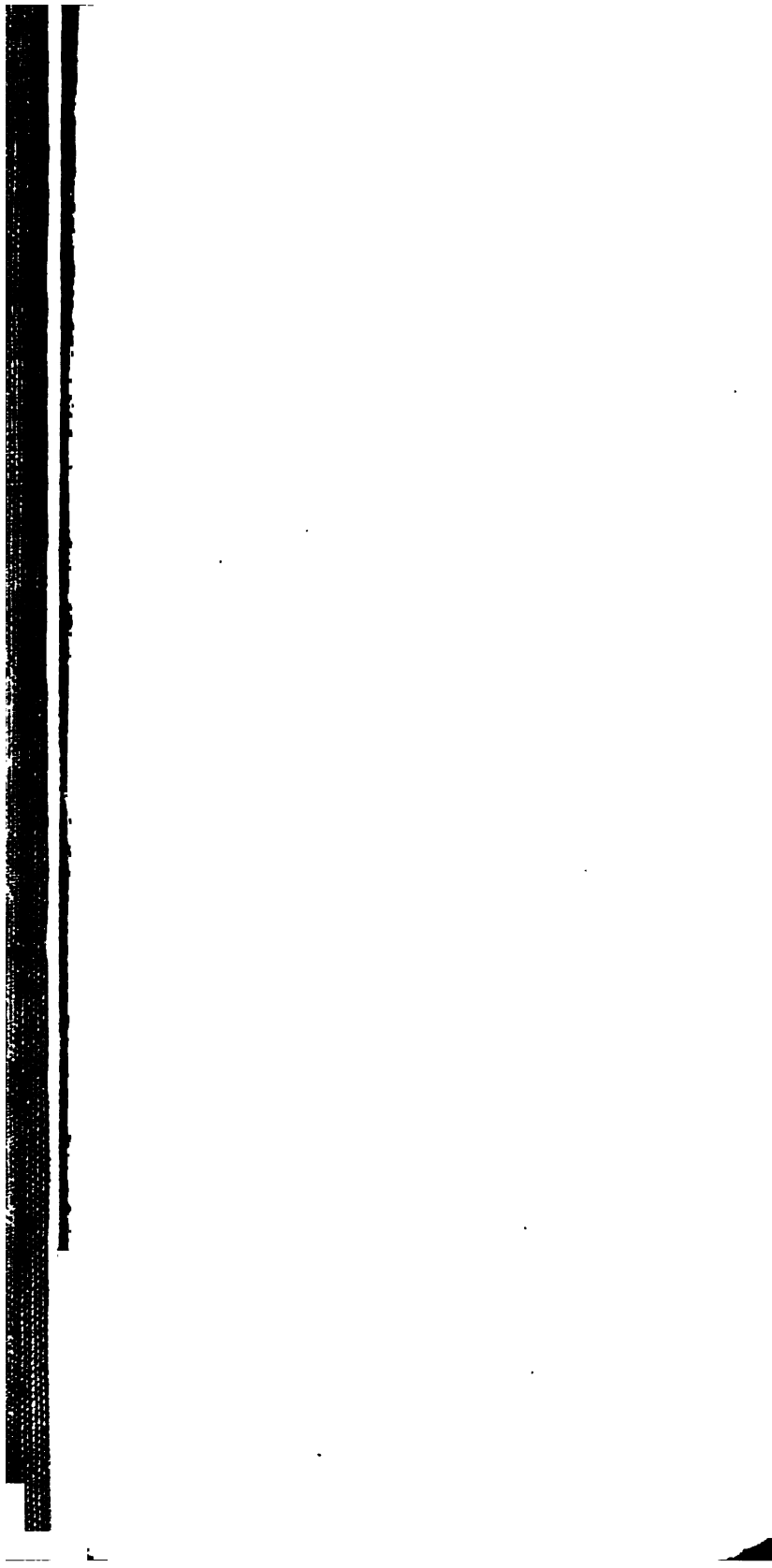

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PREFACE

In this volume are the papers and discussions on Non-ferrous Metallurgy and Metallography that were presented at the Chicago and Philadelphia meetings, 1919, the Lake Superior and Columbus meetings, 1920, and the New York meetings of 1920 and 1921. Proceedings of the meetings of the Institute of Metals Division in Philadelphia and Columbus are also included.

CONTENTS

PROCEEDINGS

PAGE

Philadelphia Meeting, October, 1919 vii
Columbus Meeting, October, 1920 viii

PAPERS

Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium. By P. D. MERICA, R. G. WALTENBERG and J. R. FREEMAN, JR. (With Discussion) 3
Simplification of Inverse-rate Method for Thermal Analysis. By PAUL D. MERICA 26
Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, Nickel and Manganese. By P. D. MERICA, R. G. WALTENBERG and A. N. FINN (With Discussion) . . 29
Heat Treatment and Constitution of Duralumin. By P. D. MERICA, R. G. WALTENBERG and H. SCOTT (With Discussion) 41
Water and Chlorides in Cement Copper Briquettes. By EDWARD KELLER . . 80
Electrolytic Zinc. By C. A. HANSEN (With Discussion) 85
Deterioration of Nickel Spark-plug Terminals in Service. By HENRY S. RAWDON and A. I. KRYNITZKY (With Discussion) 129
Grain Growth in Alpha Brass. By F. G. SMITH (With Discussion) 159
Electric-resistance Furnace of Large Capacity for Zinc Ores. By CHARLES H. FULTON (With Discussion) 188
Tin Fusible Boiler-plug Manufacture and Testing. By L. J. GUREVICH and J. S. HROMATKO (With Discussion) 227
Manufacture and Electrical Properties of Constantan. By F. E. BASH 239
Manufacture and Electrical Properties of Manganin. By F. E. BASH (With (Discussion 261
Heat Treatment of Aluminum-alloy Castings. By ZAY JEFFRIES and W. A. GIBSON (With Discussion) 270
Influence of Heat Treatment on Gun Metal. By C. F. SMART (With Discussion). 293
Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod. By C. H. MATHEWSON, C. S. TREWIN, and W. B. FINKELDEY (With Discussion 305
Five Foundry Tests of Zinc Bronzes. By C. P. KARR (With Discussion) . . . 378
Physical Properties of Nickel. By DAVID H. BROWNE and JOHN F. THOMPSON (With Discussion) 387
Physical Properties of Certain Lead-zinc Bronzes. By HOMER F. STALEY and C. P. KARR (With Discussion) 420
Relationship of Physical and Chemical Properties of Copper. By FRANK L. ANTISELL (With Discussion) 432

A Peculiar Type of Intercrystalline Brittleness of Copper. By HENRY S. RAWDON and S. C. LANGDON (With Discussion) 439
Intercrystalline Brittleness of Lead. By HENRY S. RAWDON (With Discussion). 443
Charpy Impact Test as Applied to Aluminum Alloys. By E. H. DIX, JR. (With Discussion) 466
New Process for Making Fifteen Per Cent. Phosphor-copper. By P. E. DEMMLER (With Discussion) 483
Transition Phenomena in Amalgams. By ARTHUR W. GRAY (With Discussion). 488
Physical Tests on Sheet Nickel Silver. By WM. B. PRICE and PHILIP DAVIDSON (With Discussion) 510
Colloidal State in Metals and Alloys. By JEROME ALEXANDER (With Discussion.) 524
Nickel-chromium Alloys. By LEON O. HART. 554
Treating Antimony Ores. By GEORGE P. HULST. 566
Chemical and Electrochemical Problems Involved in New Cornelia Copper Co.'s Leaching Process. By HENRY S. MACKAY (With Discussion). . . . 568
Reverberatory Furnace for Treating Converter Slag at Anaconda. By FREDERICK LAIST and H. J. MAGUIRE (With Discussion). 585
Volatilization in Assaying. By FREDERIC P. DEWEY (With Discussion). . . . 601
Coal-pulverizing Plant at Nevada Consolidated Copper Smelter. By R. E. H. POMEROY (With Discussion). 618
Laboratory Testing of Sands, Cores and Core Binders. By F. L. WOLF and A. A. GRUBB (With Discussion) 630
Coke and Byproducts as Fuels for Metals Melting. By F. W. SPERR, JR. . . . 640
Reclamation of Metal from Brass-foundry Refuse. By F. L. WOLF and G. E. ALDERSON (With Discussion) 650
Investigation of Brass Foundry Fluxes. By C. W. HILL, T. P. THOMAS, W. B. VIETZ (With Discussion) 662
Roasting and Chloridizing of Bolivian Silver-tin Ores. By M. G. F. SÖHNLEIN. (With Discussion) 676
Electrolytic Zinc Plant of Anaconda Copper Mining Co., at Great Falls, Mont. By FREDERICK LAIST, F. F. FRICK, J. O. ELTON and R. B. CAPLES (With Discussion). 699
Tooele Flue-type Cottrell Treater. By A. B. YOUNG (With Discussion). . . . 764
Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals. By W. P. SYKES (With Discussion). . . . 780
Treatment Tests on Ores of Consolidated Coppermines Co. By ROBERT LINTON (With Discussion). 816
Steel Chimneys and Their Linings at Copper Smelting Plants. By A. G. MCGREGOR (With Discussion). 830
Biographical Notice of JOHN STEWART MACARTHUR. 840

INSTITUTE OF METALS DIVISION MEETINGS

PHILADELPHIA, SEPTEMBER, 1919

The meeting of the Institute of Metals Division was held in Philadelphia from Sept. 30 to Oct. 2, 1919, inclusive. On Monday evening preceding the meeting, a dinner was held at the Ritz-Carlton Hotel at which many of the former officers of the Division and of the present officers and executive committee were present. The subject of a membership committee was discussed and a motion to appoint such a committee with powers to go over the membership list for the selection of divisional members and to institute plans for additional members was passed. Mr. H. E. Howe and Dr. Johnston of the National Research Council attended the meeting and presented their plans for an Alloys Research Association. Many opinions were voiced as to the practicability of such a scheme and Mr. Howe expressed himself in appreciation of the coöperative thought and efforts given him.

On Tuesday morning the Institute of Metals Division joined sessions with the American Foundrymen's Association and listened to the opening addresses. In the afternoon a boat ride was taken on the Delaware River, visiting the plants of the Cramp Ship and Engine Building Co. and the shipyard of the Emergency Fleet Corpn. at Hog Island. The launching of the boat christened "Afoundria" at 5 p.m. was witnessed by members of the party.

The opening technical session was held on Tuesday evening at the Ritz-Carlton Hotel at 8 o'clock, Mr. W. M. Corse presiding. The next session was held at the Ritz-Carlton at 10 o'clock on Wednesday morning and the final session at the same time and place on Thursday morning. Mr. W. H. Bassett presided on Wednesday morning and Mr. W. B. Price on Thursday. The sessions were well attended and the discussion was good. The highly technical nature of some of the papers on the program was of special note. Taken as a whole the meeting was one of the most successful ever held. The following papers were presented:

Manufacture and Electrical Properties of Manganin. By F. E. Bash.

Grain Growth in Alpha Brass. By F. G. Smith. Illustrated by lantern slides.

Five Foundry Tests of Zinc Bronzes. By C. P. Karr.

Manufacture and Electrical Properties of Constantan. By F. E. Bash.

Tin Fusible Boiler Plug Manufacture and Testing. By L. J. Gurevich and J. S. Hromatko.

Heat Treatment of Aluminum Alloy Castings. By Zay Jeffries and W. A. Gibson.

Influence of Heat Treatment on Gun Metal. By C. F. Smart.

Deterioration of Nickel Spark-plug Terminals in Service. By Henry S. Rawdon and A. I. Krynitsky.

Heat Treatment of Duralumin. By Paul D. Merica, R. G. Waltenberg and H. Scott.

Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, Nickel and Manganese. By Paul D. Merica, R. G. Waltenberg and A. N. Finn.

Simplification of Inverse-rate Method for Thermal Analysis. By Paul D. Merica.

Constitution and Metallography of Aluminum and its Light Alloys with Copper and with Magesnium. By Paul D. Merica, R. G. Waltenberg and J. R. Freeman, Jr.

Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod. By C. H. Mathewson, C. S. Trewin and W. H. Finkeldey.

Physical Properties of Certain Lead-Zinc Bronzes. By Homer F. Staley and C. P. Karr.

Physical Properties of Nickel. By David H. Browne and John F. Thompson.

Columbus, October, 1920

The meeting of the Institute of Metals Division of the A. I. M. E. with the American Foundrymen's Association in Columbus, Ohio, during the week of Oct. 4, 1920, was in every way satisfactory. The American Foundrymen's Association gave most cordial coöperation and assistance and the members of the Institute of Metals Division who were responsible for the arrangements of the meeting felt very appreciative of this help. There was a total registration of 73 members and guests.

The Executive Committee of the Institute of Metals Division met at dinner on Tuesday evening, Oct. 5. At this meeting the Messrs. Clamer, Jones, and Patch were appointed as a Nominating Committee. On Thursday, Oct. 7, this Committee announced the following nominations for officers of the Institute of Metals Division for next year: chairman, W. H. Bassett; secretary, W. M. Corse; executive committee, W. B. Price, H. J. Roast, P. D. Merica, C. H. Bierbaum, George K. Elliott, W. K. Frank, P. E. McKinney, C. H. Mathewson, W. A. Cowan, F. L. Wolf.

The Foundrymen's Exhibit was exceedingly interesting, and larger than in former years, there being between two and three hundred firms represented, covering a wide range of materials and subjects.

The Institute of Metals Division held three technical sessions, two of which were joint sessions with the A. F. A., as follows:

Tuesday, Oct. 5

Joint Session with American Foundrymen's Association

Investigation of Brass-foundry Fluxes. By C. W. Hill, T. P. Thomas and W. B. Vietz. Presented by Mr. Thomas.

Laboratory Testing of Sands, Cores and Core-binders. By F. L. Wolf and A. A. Grubb. Presented by Mr. Grubb.

Reclamation of Metal from Brass-foundry Refuse. By F. L. Wolf and G. E. Alderson. Presented by Mr. Alderson.

New Process for Making Fifteen Per Cent. Phosphor-copper. By P. E. Demmler. Presented by the author.

Recent Developments in Die-castings. By Chas. Pack.

The Solubility of Hydrogen in Molten Copper and Copper Alloys. By C. W. Hill, T. P. Thomas and G. P. Luckey. Presented by Mr. Thomas.

Wednesday, Oct. 6

Joint Session with American Foundrymen's Association

Problems of the Brass Foundryman. By Russell R. Clarke.

Casting Losses in the Aluminum Foundry. By R. J. Anderson.

Coke and Byproducts as Fuels for Metals Melting. By F. W. Sperr, Jr. Presented by Doctor Merica.

New Electric Furnace for Melting Brass. By C. H. Booth.

Status of the Electric Furnace in Non-ferrous Industries. By E. F. Cone.

Thursday, Oct. 7

Charpy Impact Test as Applied to Aluminum Alloys. By E. H. Dix, Jr. Presented by the author.

Colloidal State in Metals and Alloys. By Jerome Alexander. Presented by Mr. Archer.

Transition Phenomena in Amalgams. By A. W. Gray.

Physical Tests on Sheet Nickel Silver. By W. B. Price and P. Davidson. Presented by Mr. Davidson.

Nickel-chromium Alloys. By Leon O. Hart. Presented by Professor Hunter.

Copper Crusher Cylinders. By A. I. Krynitzky.

PAPERS

Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium*

BY P. D. MERICA,† PH. D., R. G. WALTENBERG,‡ B. S., AND J. R. FREEMAN, JR.,‡ B. S.
WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

CONTENTS

	PAGE
Constitution of Commercial Aluminum	4
Solubility of $CuAl_2$ in Aluminum at Different Temperatures	9
Effect of Magnesium on Solubility of $CuAl_2$ in Aluminum	15
Solubility of Mg_4Al_3 in Aluminum at Different Temperatures	15
Solubility of Metals and Metal Compounds in Aluminum	20
Summary and Conclusions	20

ALUMINUM and its alloys have been the subject of much investigation[1] during recent years, in the course of which the principal features of the constitution of most of the binary alloy systems with aluminum have been determined.

Except in the case of a few metals—silicon, bismuth, cadmium, lead, zinc, and tin—an aluminum-rich compound is formed in each binary system, which forms a eutectic with the aluminum or its solid solution with this compound. Thus such compounds as $FeAl_3$, $CuAl_2$, Mg_4Al_3, and $NiAl_3$ are formed, which are found in aluminum-rich alloys of their respective series as eutectics with the aluminum solid solution. These compounds are, in all cases, hard and brittle and their presence affects profoundly the physical properties of the alloys in which they occur. Within the zinc-aluminum system a compound, Al_2Zn_3, is formed that decomposes at lower temperatures.

Silicon and tin each form a simple eutectiferous series with aluminum; bismuth, lead, and cadmium are only partly miscible in the liquid state with it.

The extent of the solubility in aluminum, in solid solution, of these compounds or of the elements themselves, in the case of those series in which compounds are not formed, is of the greatest importance in

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* Published also as Bureau of Standards *Sci. Paper* 337 (1919).

† Physicist, U. S. Bureau of Standards.

‡ Assistant Physicist, U. S. Bureau of Standards.

[1] Discussion and bibliography of the literature dealing with aluminum and its alloys will be found in *Circular* No. 76 of the Bureau of Standards (1919).

considering the effect of these compounds or elements upon the physical properties of aluminum-rich alloys. Whether the compound, $CuAl_2$, is dissolved in the aluminum in an aluminum-rich alloy or is in the form of a hard and brittle constituent distributed throughout the mass must be a question of primary importance in a consideration of the mechanical properties of the alloy.

Reference to the equilibrium diagrams of the binary aluminum alloys, as they are established today, shows that, with a few exceptions, the solubilities of these compounds have not been determined with any exactness; usually not at all. Only the solubility of zinc and of $CuAl_2$ in aluminum have received any attention; the former at two and the latter at only one temperature. Reference is made to these determinations below. In many other cases an estimate, at best unsatisfactory, has been made from thermal analysis of the position of the end of the eutectic horizontal line or arrest.

The authors have undertaken to determine the solubilities of a number of these compounds at different temperatures and thus to establish the missing solubility-temperature curve of these compounds in the equilibrium diagram. This paper deals with the solubility-temperature curves of $CuAl_2$ and of Mg_4Al_3, and incidentally with the solubility of $FeAl_3$ and the condition and solubility of silicon in aluminum; determinations will be reported later on the curves for $MnAl_3$ and $NiAl_3$.

Constitution of Commercial Aluminum

Commercial ingot aluminum contains from 0.2 to 0.5 per cent. each of iron and silicon as impurities, which are at least partly visible under the microscope. Figs. 1 and 2 show the microstructures of two compositions of aluminum ingot at a low magnification; the grains of aluminum are partly surrounded by particles of other constituents, the amount of which is greater in a composition having higher content of total impurities. In Figs. 4 and 5 are shown the microstructures of the same materials at higher magnification; in Fig. 3, that of a similar material.

The microstructure of aluminum and its alloys is best developed by careful grinding and polishing followed by etching with a dilute solution of sodium hydroxide; the authors prefer one of 0.1 per cent., with the addition of approximately 10 per cent. alcohol. Such a solution does not etch deeply enough to develop the grain boundaries but it does bring out quite well the various other constituents found in aluminum and its light alloys, which are often in such fine distribution that they are obliterated by heavier etching with more concentrated solutions of sodium hydroxide or of hydrofluoric acid, which are more commonly used. As much care must be used in the grinding and polishing of the

metal as in its etching in order to secure the best results. The grinding with the finer grades of emery paper must be done with the aid of

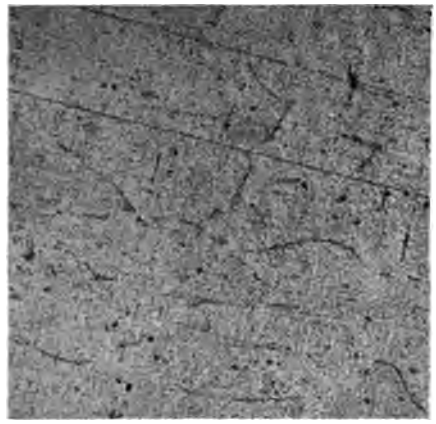

FIG. 1.

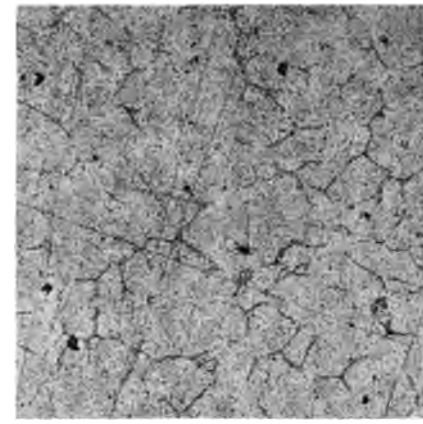

FIG. 2.

FIG. 1.—PURE ALUMINUM (AL-5) CONTAINING FE, 0.24 PER CENT., SI, 0.14 PER CENT. ETCHED WITH 0.1 PER CENT. NAOH. × 100.

FIG. 2.—COMMERCIAL INGOT ALUMINUM (AL-2) CONTAINING FE, 0.5 PER CENT., SI, 0.2 PER CENT. ETCHED WITH 0.1 PER CENT. NAOH. × 100.

some lubricant, such as paraffin, oil, or simply alcohol, and best results are obtained by polishing with alumina on suitable cloth moistened with

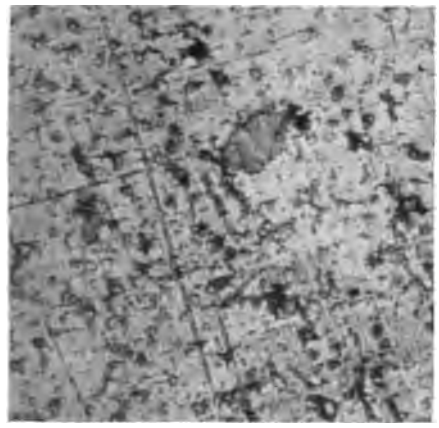

FIG. 3.

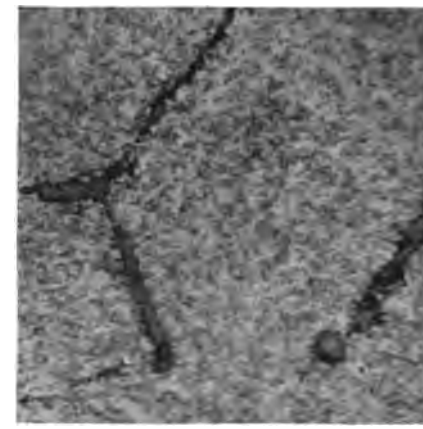

FIG. 4.

FIG. 3.—PURE ALUMINUM INGOT CONTAINING FE, 0.15 PER CENT., SI, 0.12 PER CENT., SHOWING FINE PARTICLES PROBABLY OF CONSTITUENT X. × 1500.

FIG. 4.—COMMERCIAL ALUMINUM (AL-2) SHOWING EUTECTICS OF $FeAl_3$ AND OF CONSTITUENT X. × 1000.

alcohol. The subject of the preparation of aluminum for microscopic examination is discussed in two papers by R. J. Anderson.[2,3]

[2] *Chem. & Met. Engng.* (1918) **18**, 172. [3] *Jnl.* Franklin Inst. (1919) **187**, 1.

The constitution of the binary alloys of iron with aluminum has been investigated by Gwyer.[4] The compound $FeAl_3$ forms a eutectic with aluminum at 649° C.; its composition is unknown but lies undoubtedly at a very low percentage of iron, from 1 to 2 per cent. Gwyer did not determine the solubility of $FeAl_3$ in aluminum but noted that it was very slight. The most complete investigations of the equilibrium of binary alloys of silicon and aluminum have been made by Fraenkel,[5] and by Roberts;[6] the latter investigation confirms the first in practically all respects. According to these investigations, no compound is formed in this series; the two elements form a eutectic at about 15 per cent. silicon and 576° C.; the solubility of silicon in aluminum is given as less than 0.5 per cent.

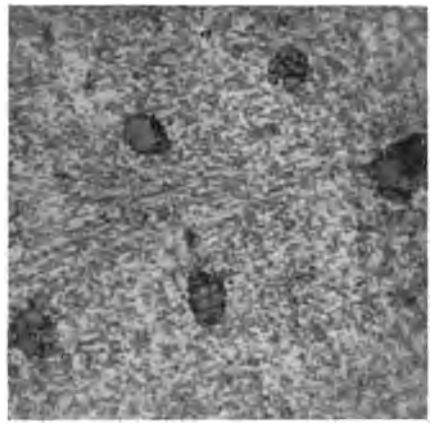

FIG. 5.

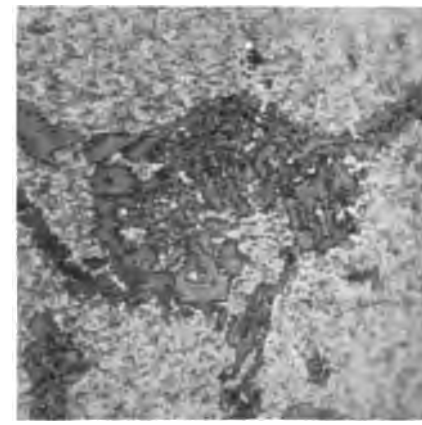

FIG. 6.

FIG. 5.—COMMERCIAL ALUMINUM (AL-2) SHOWING EUTECTICS OF $FeAl_3$ AND OF CONSTITUENT X. × 1000.

FIG. 6.—ALLOY CONTAINING 2 PER CENT. EACH OF IRON AND SILICON. THE TWO CONSTITUENTS, SI (DARK) AND $FeAl_3$ (LIGHT) ARE READILY DISTINGUISHED. × 1000.

It was necessary for the authors' work on the solubility of $CuAl_2$ and Mg_4Al_3 that they first be able to identify the various constituents that are present in alloys of aluminum with these metals. On comparing the microstructures, therefore, of several different compositions of aluminum in the light of the investigations of the equilibrium between aluminum and iron and aluminum and silicon, it was possible to identify a light bluish constituent occurring in all compositions as $FeAl_3$; this is shown in Fig. 4. In compositions having less than about 0.2 per cent. of silicon, no other constituent was noticed in the eutectic islands; in those having this amount or more of silicon a second constituent, slightly

[4] *Zeit. Anorg. Chem.* (1908) **57**, 113. [5] *Zeit. Anorg. Chem.* (1908) **58**, 154.
[6] *Trans.* Chem. Soc. (1914) **105**, 1383.

darker than the $FeAl_3$ was noticed. This is shown together with the $FeAl_3$ in Fig. 5. In order to be more certain of the identity of these two constituents of the eutectic islands, samples were prepared from a relatively pure aluminum (called Al-1) containing 0.15 per cent. iron, 0.12 per cent. silicon, and 0.02 per cent. copper, with the addition of more silicon and of more iron. Microscopic examination of these samples showed that as the silicon was increased ,the darker constituent increased, whereas as the iron was increased, the lighter constituent increased.

Fig. 6 shows the two constituents in a sample containing 2 per cent. each of iron and silicon. It was at first assumed that this darker constituent was crystallized silicon, in accordance with the equilibrium diagram. The results of thermal analyses made on 30-gm. samples of

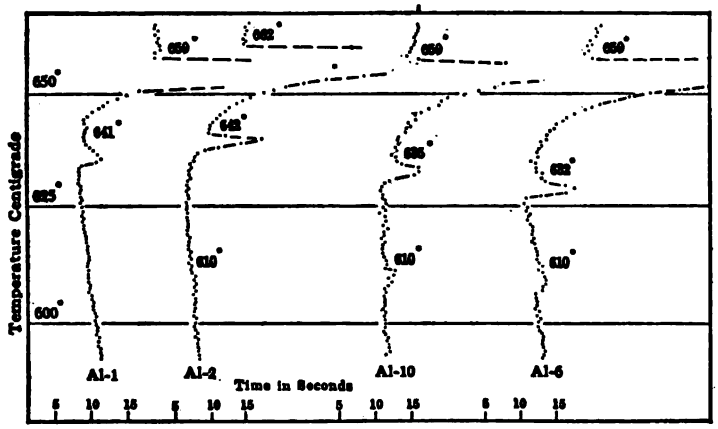

FIG. 7.—COOLING CURVES, ALUMINUM OF DIFFERENT COMPOSITIONS, SHOWING ALUMINUM–$FeAl_3$ EUTECTIC ARREST (649° C.) AND THAT OF ALUMINUM–X CONSTITUENT (610° C.). AL-1–SI, 0.12 PER CENT., FE, 0.15 PER CENT.; AL-2–SI, 0.20 PER CENT., FE, 0.50 PER CENT.; AL-10–SI, 0.24 PER CENT., FE, 0.40 PER CENT.; AL-6–SI, 0.30 PER CENT., FE, 0.60 PER CENT.

different compositions of aluminum did not bear out this conception, however.

Cooling curves of the inverse-rate type on four different compositions of aluminum are shown in Fig. 7. The temperature of the $FeAl_3$ aluminum eutectic arrest is indicated clearly on each; it is lower with increasing silicon content. The sample Al-1 containing only 0.12 per cent. of silicon showed no other arrest between this temperature and the ordinary temperature; this specimen contained only the one eutectic, that with the constituent identified as $FeAl_3$. The other compositions of higher silicon content show a lower arrest at 610° C., quite constant in temperature; the intensity of the arrest increases with the increase in silicon con-

tent. None of these compositions showed an arrest at 576° C. The appearance of the arrest at 610° C. corresponds with the appearance of the darker constituent in the eutectic in small amounts. With higher amounts of silicon, a thermal arrest is found at about 576° C. corresponding to the silicon-aluminum eutectic, and this was confirmed by the authors.

The evidence seems to point to the fact that the second and darker constituent found in the eutectic islands in aluminum is not silicon but a compound of unknown composition, either of iron and silicon alone, or of these with aluminum; it will henceforth be referred to as X(AlFeSi). The ternary liquidus surfaces must have the approximate form shown in Fig. 8. Within the area *Aluminum-abcd*, aluminum separates from the

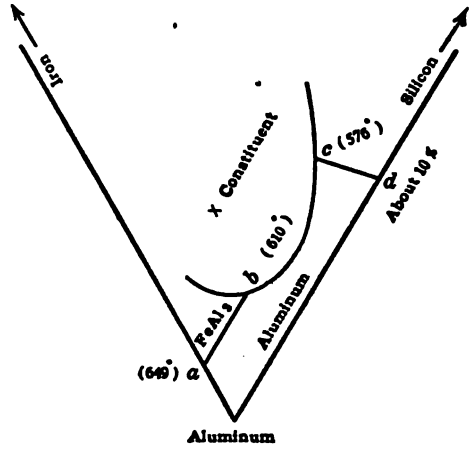

FIG. 8.—SUGGESTED FORM OF LIQUIDUS SURFACES OF TERNARY SYSTEM ALUMINUM-IRON-SILICON NEAR ALUMINUM END.

liquid; along the line *ab*, the eutectic of $FeAl_3$ and aluminum; along the line *dc*, the eutectic of silicon and aluminum; along the line *bc*, the eutectic of aluminum and the compound X; *b* and *c* are points of invariant equilibrium. This view, of course, remains to be confirmed by a necessarily much more extensive study of the ternary equilibrium; it appears at present, however, to be the only consistent interpretation of the facts.

Another feature of the structure of commercial aluminum is of the greatest interest. Figs. 3, 4, and 5 show, besides the grains of aluminum and the eutectic islands, a number of quite fine particles of some constituent scattered throughout the grains of aluminum. These are apparently particles of the constituent X and possibly also of $FeAl_3$ that have separated from the solid solution in aluminum at temperatures below the eutectic one. It was noted above that there is a slight solu-

bility of the constituent X in aluminum, since it is not found as a part of the eutectic when the silicon content is only 0.12 per cent. nor is an arrest found at 610° C. At 610°, therefore, approximately 0.12 to 0.20 per cent. of silicon as X dissolves in aluminum; at lower temperatures, its solubility diminishes and it precipitates again in much finer particles.

Little can be said as yet about the solubility of $FeAl_3$ in aluminum, as in the purest aluminum yet prepared and examined $FeAl_3$ has been found in quite appreciable quantities; this sample, Al-1, contained 0.15 per cent. of iron. Iron, as $FeAl_3$, is therefore not completely soluble in aluminum in this amount. It may be mentioned, also, that although no attempts were made to discover whether by annealing this amount of iron could be made to dissolve in commercial aluminum, it was noted in the course of the work described below, that in alloys containing besides this amount of iron about 0.5 per cent. copper, no solution of the $FeAl_3$ occurred upon annealing for 20 hr. at 500° C.

In the course of the examination and investigation of aluminum, no evidence has been found of any transformation of silicon from one form into another nor of the existence of the so-called graphitoidal silicon. The latter term originated with the analyst of aluminum and its light alloys, who finds under certain conditions that a residue is left from the action of the concentrated acids used in dissolving the sample, which is insoluble in hydrofluoric acid. It is suggested that the occurrence of the silicon in the various forms: (1) of eutectic particles of constituent X, (2) of eutectic particles of silicon, (3) of segregate particles of X, and (4) of a solid solution in aluminum, possibly explains the phenomena experienced in the analysis of the metal. Thus the silicon existing in solid solution in aluminum would undoubtedly dissolve readily in the concentrated acids to give SiO_2, whereas the particles of X or of crystallized silicon would be much less soluble.

Solubility of $CuAl_2$ in Aluminum at Different Temperatures

The equilibrium of copper-aluminum alloys has been investigated by Gwyer,[4] Carpenter and Edwards,[7] Curry,[8] Guillet,[9] Campbell and Matthews,[10] and others. Gwyer finds that 4 per cent. of copper dissolves in aluminum as $CuAl_2$. Carpenter and Edwards place the solubility at 4 per cent., Curry, at 11 per cent., and Campbell and Matthews, at 2 per cent. These values hold for the eutectic temperature 540° C.

Annealing experiments were undertaken to ascertain the course of the solubility-temperature curve. For these determinations 100 gm.

[7] *Proc.* Inst. Mech. Eng. (Jan., 1907) 57.
[8] *Jnl. Phys. Chem.* (1907) **11**, 425.
[9] *Comptes Rendus* (1905) **141**, 464.
[10] *Jnl.* Am. Chem. Soc. (1902) **24**, 253.

melts of different compositions of copper-aluminum alloys, varying from 0.5 to 5.0 per cent. of copper, were made in a small gas furnace; the purest

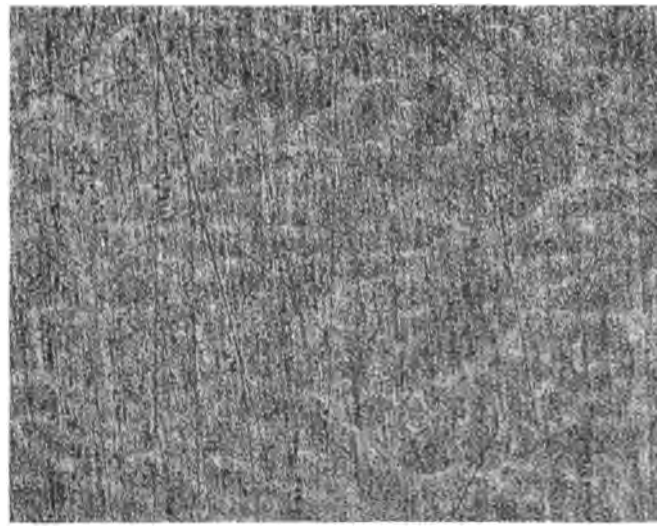

FIG. 9.—ALLOY C-20 AS CAST, SHOWING EUTECTIC OF $CuAl_2$.—ALUMINUM. CU, 0.5 PER CENT. × 100.

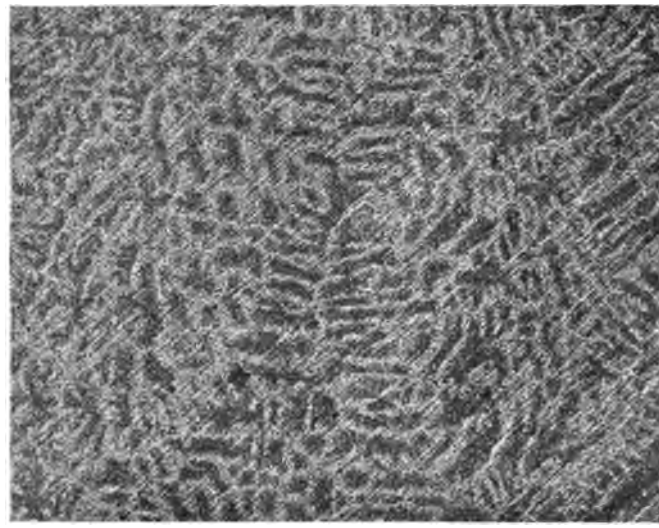

FIG. 10.—ALLOY C-29 AS CAST, SHOWING EUTECTIC OF $CuAl_2$.—ALUMINUM. CU, 5.1 PER CENT. × 100.

aluminum available, namely Al-1, was used. The resulting alloys were cast in chill molds, ½ in. (12.7 mm.) in diameter. Figs. 9 and 10 show

the typical structures of these alloys as chill cast in this form. Free $CuAl_2$ was observed even in the cast specimen C-20 containing 0.5 per cent. copper. The compositions of the cast alloys are given in Table 1.

The $CuAl_2$ can readily be distinguished from the $FeAl_3$ particles by the fact that they are much whiter in natural color and that they do not turn brown upon etching for several minutes with 0.1 per cent. NaOH, as does $FeAl_3$.

Specimens of these alloys were annealed for 20 hr. at 525°, 500°, 400°, and 300° C., quenched in water from these temperatures, and examined microscopically for the presence of free $CuAl_2$. The results of these examinations are given in Table 1. A series of photomicrographs, Figs. 11 to 14, show the microstructures of alloys C24-B to C27-B after annealing at 500° C. and quenching. $CuAl_2$ is found in C27-B (3.8 per cent. Cu) and C26-B (3.6 per cent. Cu) but not in C25-B (3.1 per cent. Cu) and C24-B (2.5 per cent. Cu).

To observe whether 20 hr. annealing was really sufficient to bring about equilibrium within these alloys, specimens of C20 to C25 (and marked H) were annealed 10 days at 400° C. and quenched. The results of examination showed that C23-H contained a small amount of $CuAl_2$ and C22-H, none, in exact agreement with observations after 20 hr. annealing at the same temperature.

A curious fact was noticed in the annealing of these alloys. Once the $CuAl_2$ has dissolved in the aluminum, it precipitates again from super-

TABLE 1.—*Microscopic Examination for Presence of Free $CuAl_2$ in Annealed Chill-cast Copper-aluminum Alloys. All Specimens Were Quenched in Water After Annealing*

Number of Alloy	Per cent. of Copper	Results of Microscopic Examination to Determine Whether Free $CuAl_2$ was Present after Annealing			
		Annealed at 525° C. Marked G	Annealed at 500° C. Marked B	Annealed at 400° C. Marked A	Annealed at 300° C. Marked C
C-20	0.5	No $CuAl_2$	No $CuAl_2$	No $CuAl_2$	No $CuAl_2$
C-21	1.1	No $CuAl_2$	No $CuAl_2$	No $CuAl_2$	No $CuAl_2$
C-22	1.6	No $CuAl_2$	No $CuAl_2$	No $CuAl_2$	Small amount
C-23	2.1	No $CuAl_2$	No $CuAl_2$	Small amount	Much $CuAl_2$
C-24	2.5	No $CuAl_2$	No $CuAl_2$	Much $CuAl_2$	Much $CuAl_2$
C-25	3.1	No $CuAl_2$	No $CuAl_2$	Much $CuAl_2$	Much $CuAl_2$
C-26	3.6	No $CuAl_2$	Small amount	Much $CuAl_2$	Much $CuAl_2$
C-27	3.8	One or two particles only	Much $CuAl_2$	Much $CuAl_2$	Much $CuAl_2$
C-28	4.5	Small amount	Much $CuAl_2$	Much $CuAl_2$	Much $CuAl_2$
C-29	5.1	Much $CuAl_2$	Much $CuAl_2$	Much $CuAl_2$	Much $CuAl_2$

saturated solutions only with difficulty, or perhaps more accurately stated, it apparently precipitates from such solutions, but in particles of very high dispersion or small size, and these particles coalesce into

larger ones only with difficulty. Specimens of the C20 to C29-B series, which had been annealed 20 hr. at 500° C. and quenched, were reannealed and quenched from lower temperatures as follows: C20 to C29-B-1,

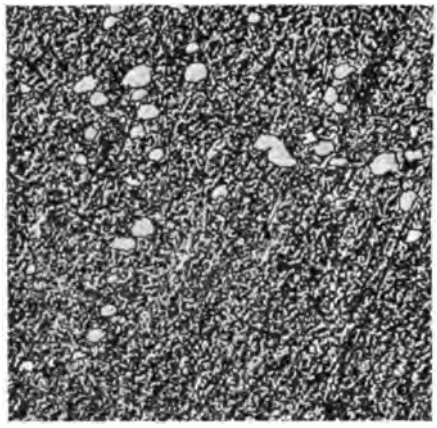

FIG. 11.

FIG. 12.

FIG. 11.—ALLOY C27–B. CU, 3.8 PER CENT. ANNEALED AND QUENCHED FROM 500° C. × 300.

FIG. 12.—ALLOY C26–B. CU, 3.6 PER CENT. ANNEALED AND QUENCHED FROM 500° C. × 300.

at 320° C. for 45 hr. and C20 to C29-B-2, at 400° C. for 20 hr. Reannealing caused apparently no change in the structure of any of the alloys; at

FIG. 13.

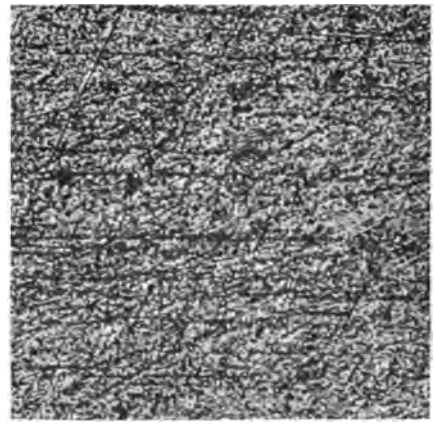

FIG. 14.

FIG 13.—ALLOY C25–B. CU, 3.1 PER CENT. ANNEALED AND QUENCHED FROM 500° C. × 300.

FIG. 14.—ALLOY C24–B. CU, 2.5 PER CENT. ANNEALED AND QUENCHED FROM 500° C. × 300.

least, no particles of $CuAl_2$ of a size comparable with the original eutectic generation reappeared in those samples to correspond with the diminu-

tion of solubility at the lower temperatures. Fig. 15 shows the structure of C25-B-1, which may be compared with Figs. 11 to 14.

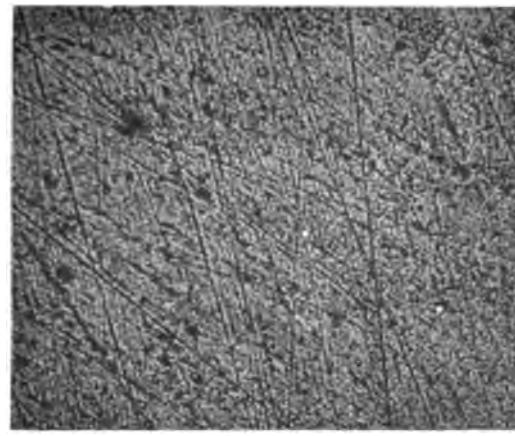

FIG. 15.—ALLOY C25–B-1, ANNEALED 20 HR. AT 500° C., QUENCHED, REANNEALED 45 HR. AT 320° C., AND QUENCHED. NO PARTICLES OF $CuAl_2$ ARE VISIBLE AT THIS MAGNIFICATION. CU, 3.1 PER CENT. × 300.

Only upon very slow cooling through the temperature range 500° to 300° C. do segregate or precipitated particles of $CuAl_2$ coalesce to such an

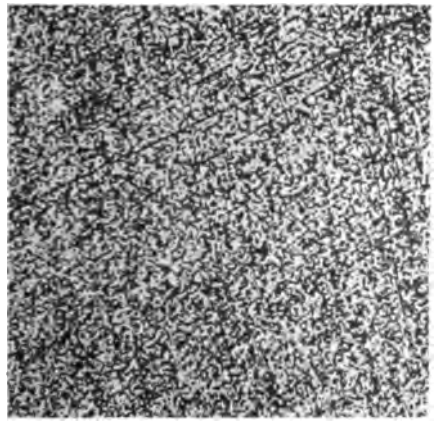

FIG. 16.

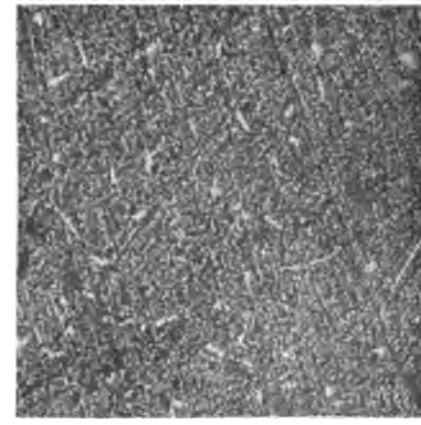

FIG. 17.

FIG. 16.—SPECIMEN C25–B. ANNEALED AT 500° C., AND QUENCHED. CU, 3.1 PER CENT. × 300.

FIG. 17.—SAME AREA OF C25–B AS SHOWN IN FIG. 16, BUT AFTER REHEATING TO 500° C. AND SLOWLY COOLING. $CuAl_2$ HAS PRECIPITATED AND COALESCED. × 300.

extent that they may readily be identified as such. Specimens of C25-B and of E13-B that had been annealed at 500° C. were reheated to 500° C.

and cooled from that temperature very slowly to room temperature. The furnace cooled from 500° to 345° C. in 15 hr. Areas were marked off on both specimens before this final treatment and examined before and after heating and cooling. As annealed and quenched, no $CuAl_2$, corresponding to the equilibrium solubility, was found in either of the specimens; after heating to 500° C. and cooling at this slow rate, $CuAl_2$ particles of fairly large size were found in both specimens in profusion. Figs. 16 and 17 show an area of C25-B before and after heating and slow cooling respectively.

Samples of alloys E9 to E11 were annealed for various periods of

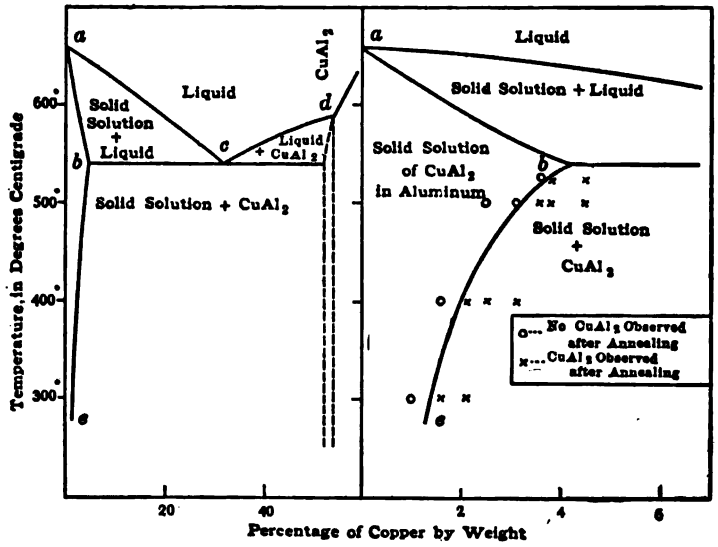

FIG. 18.—PORTION OF THE EQUILIBRIUM DIAGRAM OF THE COPPER-ALUMINUM ALLOY SERIES SHOWING THE SOLUBILITY CURVE $CuAl_2$ IN ALUMINUM.

time at 400° C. to determine what period was necessary to produce equilibrium between the $CuAl_2$ and solid solution. The results of these experiments are given in Table 2. At 400° C., equilibrium was attained in these small chill cast specimens after 30 min.; after that period no further change took place.

In Fig. 18 are shown the results of these solubility determinations. There is given the aluminum side of the equilibrium diagram of copper and aluminum, of which the portion *be* has been determined by the above experiments; the remainder is taken from the results of previous investigations. The solubility of $CuAl_2$ decreases with decreasing temperature from about 4 per cent. at 525° C. to about 1 per cent. at 300° C., and is apparently still diminishing at lower temperatures.

TABLE 2.—*Microscopic Examination for Presence of Free $CuAl_2$ in Samples of Chill-cast Copper-aluminum Alloys Annealed at 400° C. and Quenched*

Number of Sample	Per cent., Copper	Period of Annealing	Temperature of Annealing	Examination for Presence of Free $CuAl_2$
E9-A	1.0	15 min.	400° C.	Small amount of $CuAl_2$
E10-A	1.5	15 min.	400° C.	Considerable $CuAl_2$
E9-B	1.0	30 min.	400° C.	No $CuAl_2$
E10-B	1.5	30 min.	400° C.	Very small amount of $CuAl_2$
E11-B	1.9	30 min.	400° C.	Much $CuAl_2$
E10-C	1.5	60 min.	400° C.	No $CuAl_2$
E11-C	1.9	60 min.	400° C.	Small amount of $CuAl_2$
E10-E	1.5	13 hr.	400° C.	No $CuAl_2$
E11-E	1.9	13 hr.	400° C.	Small amount of $CuAl_2$

Effect of Magnesium on Solubility of $CuAl_2$ in Aluminum.—In seeking an explanation for the effect of magnesium on the physical properties of heat-treated duralumin,[11] the question presented itself whether the solubility-temperature curve of $CuAl_2$ in aluminum was displaced by the presence of the usual small amounts of magnesium. Specimens were chill cast and contained:

Specimen	Copper, Per Cent.	Magnesium, Per Cent.	Specimen	Copper, Per Cent.	Magnesium, Per Cent.
C30	1	0.5	C34	1	1.0
C31	2	0.5	C35	2	1.0
C32	3	0.5	C36	3	1.0
C33	4	0.5	C37	4	1.0

These were examined after annealing 20 hr. at 500° C. followed by quenching. Specimens C32-B and C36-B contained, after this annealing, no free $CuAl_2$, whereas specimens C33-B and C37-B did. Apparently as much as 1 per cent. of magnesium does not affect appreciably the temperature-solubility curve of $CuAl_2$ in aluminum.

SOLUBILITY OF Mg_4Al_3 IN ALUMINUM AT DIFFERENT TEMPERATURES

The equilibrium of magnesium-aluminum alloys has been studied by Schirmeister,[12] Wilm,[13] and Grube.[14] Schirmeister finds no eutectic arrest for the eutectic of Mg_4Al_3-aluminum at 1 per cent. magnesium;

[11] See footnote 16.
[12] *Metall u. Erz.* (1914) **2**, 522.
[13] *Metallurgie* (1911) **8**, 225.
[14] *Zeit. Anorg. Chem.* (1905) **45**, 225.

Grube makes no comment on the amount of Mg_4Al_3 that may be soluble in aluminum.

For the authors' determinations, samples of magnesium-aluminum

FIG. 19.

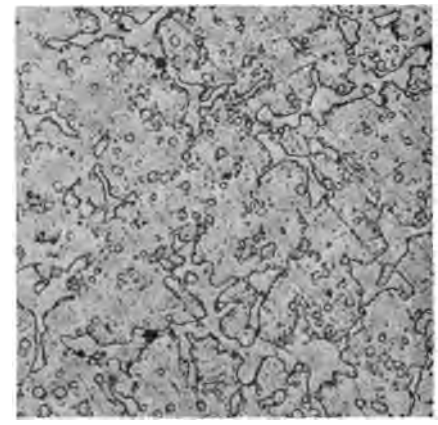

FIG. 20.

FIG. 19.—MAGNESIUM-ALUMINUM ALLOY A38 AS CHILL CAST. Mg, 17.8 PER CENT. ETCHED WITH 5.0 PER CENT. NaOH. × 300.

FIG. 20.—MAGNESIUM-ALUMINUM ALLOY, ANNEALED 20 HR. AT 400° C. AND THEN QUENCHED. A37-400. Mg, 17.1 PER CENT. ETCHED WITH 5 PER CENT. NaOH. × 300.

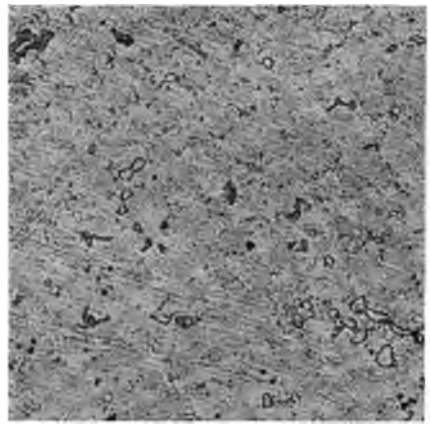

FIG. 21.

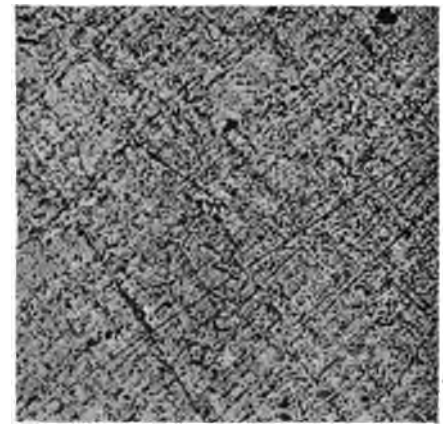

FIG. 22.

FIG. 21.—MAGNESIUM-ALUMINUM ALLOY, ANNEALED 20 HR. AT 400° C. AND THEN QUENCHED. A27-400. Mg, 13.2 PER CENT. ETCHED WITH 5 PER CENT. NaOH. × 300.

FIG. 22.—MAGNESIUM-ALUMINUM ALLOY, ANNEALED 20 HR. AT 400° C. AND THEN QUENCHED. A36-400. Mg, 11.7 PER CENT. ETCHED WITH 5 PER CENT. NaOH. × 300.

alloys were prepared in the same manner as were those for the previous series. Table 3 gives the compositions of the alloys so prepared and Fig. 19 shows the typical duplex structure of one of the chill-cast alloys, A38.

Specimens of the alloys were annealed for 20 hr. at 450, 400, and 300° C., and then quenched. The microstructure was developed by etching with

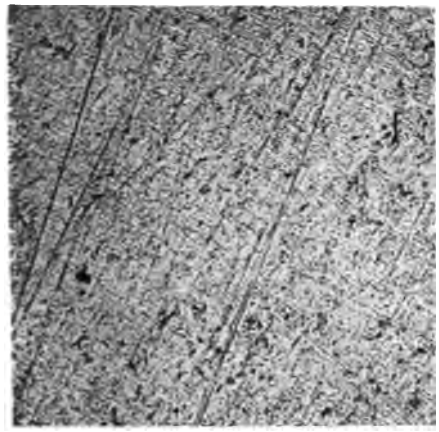

FIG. 23.

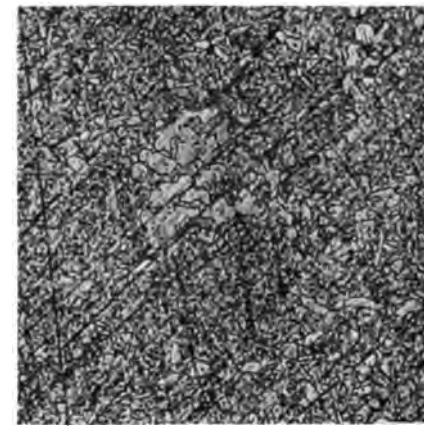

FIG. 24.

FIG. 23.—A35-450. Mg, 12.2 PER CENT. QUENCHED. × 300.
FIG. 24.—A35-450A. Mg, 12.2 PER CENT. SLOWLY COOLED. × 300.

Magnesium-aluminum alloy A35-450, which contains no Mg_4Al_3 after annealing at 450° C. and quenching (Fig. 23), but in which Mg_4Al_3 precipitates upon reheating to 420° C. and slowly cooling (Fig. 24).

5 per cent. NaOH solution and the specimens were examined for the presence of free Mg_4Al_3. Table 3 gives the results of these determina-

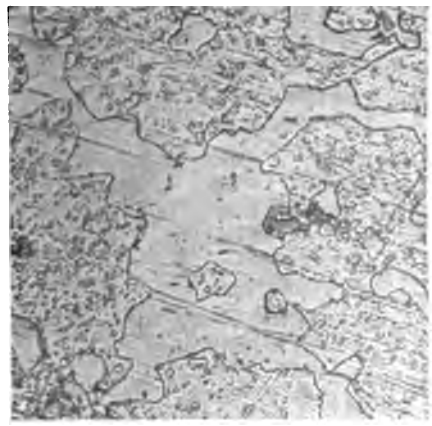

FIG. 25.

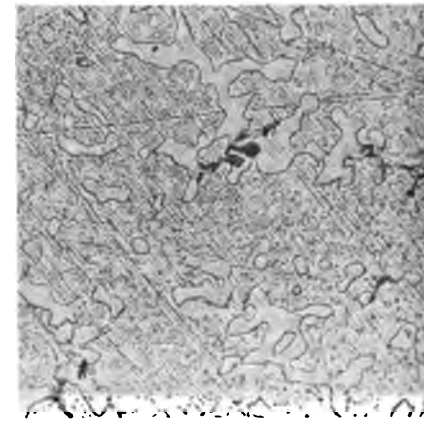

FIG. 26.

FIG. 25.—A35-300. Mg, 12.2 PER CENT. × 500.
FIG. 26.—A37-300. Mg, 17.1 PER CENT. × 500.

Magnesium-aluminum alloys annealed at 300° C., showing the deep blue constituent (dark in photograph).

tions. Figs. 20 to 22 show typical microstructures for a series annealed at 400° C.

TABLE 3.—*Microscopic Examination for Presence of Free Mg_4Al_3 in Annealed Chill-cast Magnesium-aluminum Alloys. All Specimens Were Quenched in Water after Annealing*

Number of Alloy	Per cent. of Magnesium	Results of Microscopic Examination Whether Free Mg_4Al_3 was Present After Annealing		
		Annealed at 450° C., Marked −45	Annealed at 400° C., Marked −4	Annealed at 300° C., Marked −3
A-31	5.9	No Mg_4Al_3	No. Mg_4Al_3	Small amount Mg_4Al_3
A-32	6.9	No Mg_4Al_3	No. Mg_4Al_3	Much Mg_4Al_3
A-34	9.1	No Mg_4Al_3	No. Mg_4Al_3	Much Mg_4Al_3
A-36	11.7	No Mg_4Al_3	No. Mg_4Al_3	Much Mg_4Al_3
A-35	12.2	No Mg_4Al_3	No. Mg_4Al_3	Much Mg_4Al_3
A-27	13.2	Small amount Mg_4Al_3	Small amount Mg_4Al_3	Much Mg_4Al_3
A-37	17.1	Much Mg_4Al_3	Much Mg_4Al_3	Much Mg_4Al_3
A-38	17.8	Much Mg_4Al_3	Much Mg_4Al_3	Much Mg_4Al_3

The solubility of Mg_4Al_3 in aluminum decreases with lowering of the temperature exactly as in the case of $CuAl_2$. Specimens of A35-450 and of A36-450 annealed 20 hr. at 450° C. and quenched were reheated to

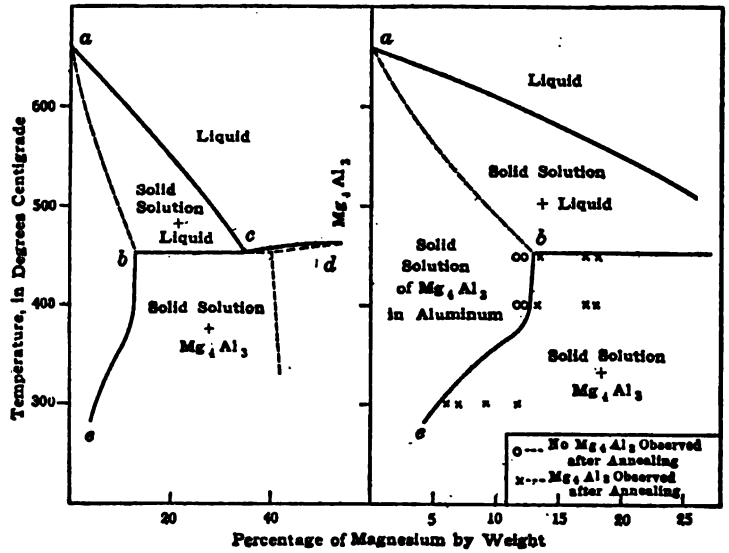

FIG. 27.—PORTION OF THE EQUILIBRIUM DIAGRAM OF THE MAGNESIUM-ALUMINUM ALLOY SERIES SHOWING THE SOLUBILITY CURVE Mg_4Al_3 IN ALUMINUM.

420° C. and allowed to cool very slowly in the furnace. The furnace cooled from 420° to 260° in 24 hr. In these specimens previously free from Mg_4Al_3, this second heat treatment caused a copious precipitate of this constituent. Figs. 23 and 24 show the structure of A35-450 before and after slow cooling respectively.

The results of these determinations are shown in Fig. 27, in which is reproduced a portion of the equilibrium diagram, as determined by Grube, for the magnesium-aluminum alloys and in which is inserted the portion *be* determined by the above experiments.

In aluminum-rich alloys of magnesium with commerical aluminum, besides the two constituents or phases aluminum solid solution and Mg_4Al_3, another constituent is invariably found, the amount of which seems to increase slowly, if at all, with an increase of the magnesium content beyond about 1 per cent. It has a deep blue color and is easily distinguished from the other two constituents mentioned and from the $FeAl_3$,

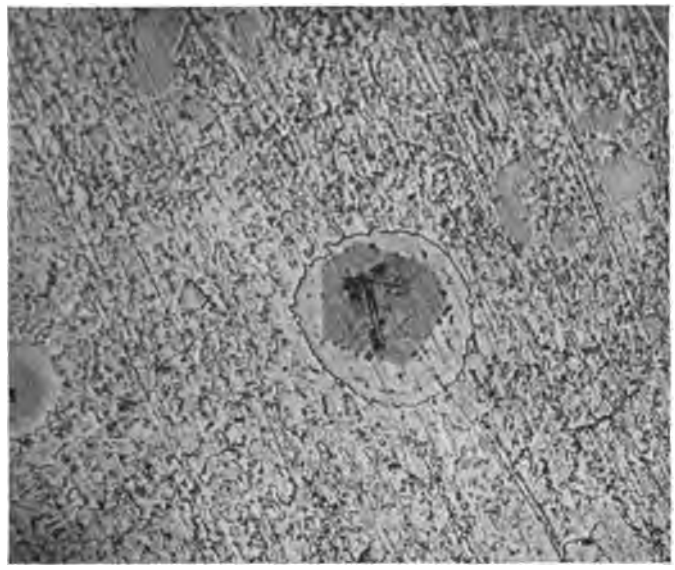

FIG. 28.—ALLOY N28 CONTAINING CU, 4.98 PER CENT., MG, 2.41 PER CENT., FE, 0.62 PER CENT., SI, 0.32 PER CENT., AND SHOWING DEEP BLUE CONSTITUENT CHARACTERISTIC OF ALUMINUM-RICH ALLOYS CONTAINING MAGNESIUM. × 1000.

which is also present. It is shown in Figs. 25 and 26. This constituent occurs in alloys also containing both copper and magnesium. Fig. 28 shows an island of $CuAl_2$ in such an alloy in which is embedded a particle of this blue constituent.

This is believed to be Mg_2Si, although the authors have no direct evidence for this belief. Vogel[15] found a very marked and definite compound Mg_2Si in his study of the binary series, magnesium-silicon, which was of a deep blue color much resembling the constituent described above. It is unlikely that this constituent is a compound of iron and magnesium since these two metals unite only with much difficulty and probably do

[15] *Zeit. Anorg. Chem.* (1909) **61**, 46.

not form a compound. The only other possibility, therefore, is that the constituent is a silicate or a ternary or quaternary compound containing magnesium, silicon, iron, or aluminum.

The occurrence of this constituent in light alloys of aluminum containing magnesium is believed to be of the greatest significance in connection with the effect of magnesium upon the mechanical and other physical properties of these alloys. This question is, however, discussed at greater length in another article.[16]

Solubility of Metals and Metal Compounds in Aluminum

A review of the results obtained above and of those obtained by Rosenhain and Archbutt[17] and of Bauer and Vogel[18] on the solubility of zinc in aluminum shows that a decreasing solubility in aluminum with decreasing temperature of that constituent in immediate equilibrium with the aluminum is characteristic of the metal. Thus the solubility of zinc in aluminum at 443° C. is about 40 per cent., whereas at 256° C. it is only about 25 per cent.

This form of the solubility curve is of course not unusual, yet we find in the case of equilibrium of metals many cases in which the solubility of a constituent increases with decreasing temperature. Thus, in the zinc-copper series, the solubility of the beta constituent in the alpha decreases with increasing temperature. In another article[19] the significance of the form of solubility curve characteristic of aluminum is discussed.

Summary and Conclusions

The temperature-solubility curves of $CuAl_2$ and of Mg_4Al_3 in aluminum were determined by the method of annealing and microscopic examination. Aluminum dissolves about 4.2 per cent. of copper as $CuAl_2$ at 525° C. and about 12.5 per cent. of magnesium as Mg_4Al_3 at 450° C. The solubility of both compounds decreases with decreasing temperature. At 300° C., aluminum dissolves only 1 per cent. of copper as $CuAl_2$ and slightly less than 5.9 per cent. of magnesium as Mg_4Al_3.

The structural identification of the various constituents, $FeAl_3$, $CuAl_2$, Mg_4Al_3, found in alloys with magnesium and with copper is described, and a constituent is noted in all light aluminum alloys containing magnesium which is believed to be Mg_2Si.

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[16] Merica, Waltenberg, and Scott, this volume; also *Bulletin* Bureau of Standards, 1919.

[17] *Phil. Trans.* Roy. Soc. London (1912) **A, 211,** 315.

[18] *Int. Zeit. Metallographie* (1916) **8,** 101.

[19] See footnote 16.

The solubility of iron, as $FeAl_3$, in aluminum is at all temperatures less than 0.15 per cent.

Small amounts of silicon up to from 0.12 to 0.20 per cent. are dissolved by aluminum at the eutectic temperature but are reprecipitated upon cooling corresponding to the diminished solubility for silicon of aluminum at lower temperatures.

Silicon in the usual commercial amounts is probably present as a compound of iron and silicon together with some aluminum. The composition of this compound is not known but it solidifies with aluminum and $FeAl_3$ at an invariant point at 610° C.

DISCUSSION

GEO. F. COMSTOCK* AND AUSTIN B. WILSON,* Niagara Falls, N. Y. (written discussion).—A sample of a light aluminum alloy was recently sent to this laboratory for metallographic examination. Attempts were made to identify its various hard constituents by the methods given in this paper and the conclusions thus reached were checked by the methods of Hanson and Archbutt.[20] The results obtained were most unexpected.

The sample was found, by chemical analysis, to contain 94.6 per cent. aluminum, 4.4 per cent. copper, 0.63 per cent. manganese, 0.41 per cent. iron, 0.43 per cent. magnesium, and 0.06 per cent. silicon. The polished section showed numerous irregular hard bright particles standing out in relief and a few small rounded bright particles much less conspicuous. Etching for several minutes with 0.1 per cent. NaOH was tried, to determine whether the prominent hard constituent was $CuAl_2$ or $FeAl_3$, and as it was not darkened at all, it was assumed to be the former, according to the statement on p. 11. The less prominent round spots were attacked by this etching, however, and showed very distinct light and dark stripes, indicating that they were some eutectic. The dark constituent was held to be $FeAl_3$, since the paper stated that it was darkened by this etching, but the paper gave no information concerning the constituent forming the bright stripes of this eutectic. In the descriptions of the eutectics of $FeAl_3$ and the silicon constituent called *X*, no mention is made of any etching and it is not stated whether Figs. 3, 4, 5 and 6 show etched or unetched sections. If these were etched, *X* must be darkened more by the etching than $FeAl_3$; and if only one of these constituents is present in an alloy with $CuAl_2$, the methods given in the paper would not show which one the darkened constituent really was. Furthermore, no hint is given as to any method for distinguishing Mg_4Al_3 from $FeAl_3$ or $CuAl_2$, so that the conclusion claiming the description of the "structural identification" of these constituents seems exaggerated.

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* Physical Testing Laboratory, Titanium Alloy Mfg. Co.

[20] Micrography of Aluminum and its Alloys. *Jnl.* Inst. Met. (1919) **21**, 291.

It was decided to check the identification of the prominent hard bright constituent as $CuAl_2$, by using the nitric-acid method of Hanson and Archbutt on another polished section of the same sample. A 20 per cent.

FIG. 29.—ALLOY WITH 4 4 PER CENT. COPPER, ETCHED WITH 0.1 PER CENT. NaOH, SHOWING $FeAl_3$ PARTICLES UNATTACKED, AND ROUND SPOT OF EUTECTIC, ONE OF WHOSE COMPONENTS IS DARKENED. × 700.

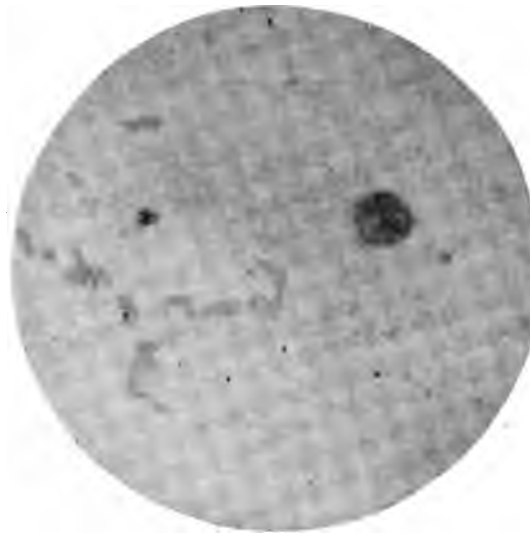

FIG. 30.—SAME ALLOY ETCHED WITH 20 PER CENT. HNO_3, SHOWING $FeAl_3$ PARTICLE UNATTACKED, AND ROUND SPOT OF EUTECTIC PARTLY DARKENED. × 700.

solution of this acid (by weight) was used for a few seconds at 70° C., which procedure is stated to turn $CuAl_2$ brown, leaving $FeAl_3$ unattacked. The prominent hard bright constituent of this alloy was plainly shown

FIG 31.—ALLOY WITH 8 PER CENT. COPPER, UNETCHED, SHOWING TWO HARD CONSTITUENTS, ONE DARKER THAN THE OTHER AND IN THE FORM OF LONG NARROW RODS. × 700.

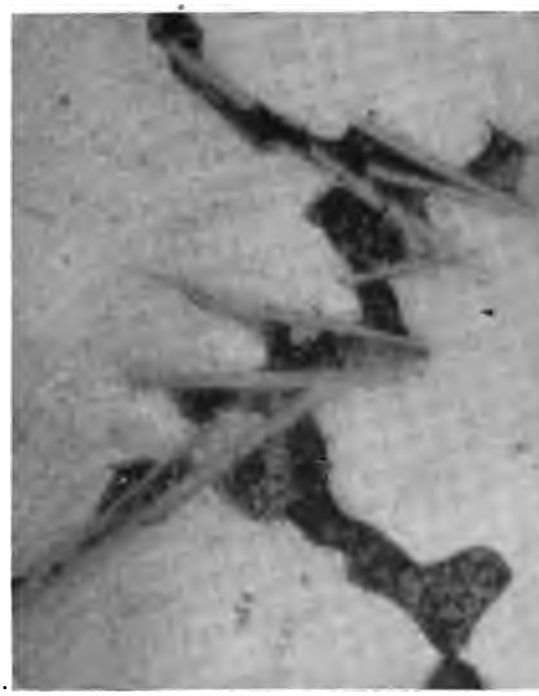

FIG. 32 —SAME SPOT AS FIG. 31, ETCHED WITH 20 PER CENT. HNO_3, SHOWING $CuAl_2$ DARKENED AND $FeAl_3$ NEEDLES UNATTACKED. × 700.

by this method to be $FeAl_3$, and the less conspicuous round particles, by partly turning brown, were shown to contain $CuAl_2$. Thus these two methods gave directly contradictory results, so it became at once a matter of interest to find out which was right.

For this purpose we took a polished section of the standard aluminum alloy with 8 per cent. copper, and etched it by each of these methods in turn. This alloy would naturally contain decidedly more $CuAl_2$ than the one first described, but would probably not have any greater iron

FIG. 33.—SAME SPOT AS FIG. 31, ETCHED WITH 0.1 PER CENT. NaOH, SHOWING $CuAl_2$ SLIGHTLY DARKENED SO AS TO BE LESS EASILY DISTINGUISHED FROM THE GRAYER $FeAl_3$ THAN BEFORE ETCHING. × 700.

content. In the unetched condition, it plainly showed two prominent hard constituents, one as white as the soft aluminum ground mass, and the other slightly more blue or gray. The latter was very similar to the prominent constituent in the 4.4 per cent. copper sample. When etched by Hanson and Archbutt's method, the grayer constituent was unattacked, meaning that it was $FeAl_3$, and the whiter hard constituent was colored brown, identifying it as $CuAl_2$. This agrees perfectly with what would be expected from the greater copper content of this sample as compared with the alloy first described. When repolished and etched with 0.1 per cent. NaOH, as advised by Merica, Waltenberg, and Free-

man, however, there was at first hardly any change in these constituents from the unetched state, but after 9 min. the whiter constituent, which must be $CuAl_2$ in this case, became slightly brownish, while the grayer $FeAl_3$ was not attacked at all, but the outlines of both against the aluminum ground mass became more prominent.

Thus the work of Hanson and Archbutt on these constituents was checked on every point, with the unavoidable corollary that the paper under discussion must be in error in regard to the distinction between $CuAl_2$ and $FeAl_3$ by etching. The data submitted by the authors on the solubility of the various compounds in aluminum is doubtless of great value, but their descriptions of the constituents and their suggestions for identifying them leave much to be desired in reliability, to say the least.

P. D. MERICA (author's reply to discussion).—The method of preparation and polishing of the sample has much to do with the manner in which the constituents of aluminum alloys will etch; this preparation requires care and experience with these alloys and probably the method of preparation used by Messrs. Comstock and Wilson was not the same as that of the authors. Although we have not had occasion to try the method of Hanson and Archbutt, which was described some time after the authors' work was completed, we are convinced that it is superior to our own; it apparently gives definite clear-cut results and a distinct differentiation between $FeAl_3$ and $CuAl_2$, which is very desirable.

It is apparently impossible to darken Mg_4Al_3 with NaOH of dilute concentrations, whereas by prolonged etching with such solutions even $CuCl_2$ is darkened; it is distinguished from $FeAl_3$ by its color in the unetched condition, being much whiter than the latter. Reference to the data contained in the original article may convince Messrs. Comstock and Wilson that it is rarely necessary to distinguish Mg_4Al_3 from $CuAl_2$ in commercial alloys, since when copper is present there is rarely over 1 per cent. of magnesium added, which is not sufficient for the formation of undissolved Mg_4Al_3, and when the latter compound is present in high percentage magnesium alloys copper is generally absent.

Simplification of Inverse-rate Method for Thermal Analysis*

BY PAUL D. MERICA,† PH. D., BAYONNE, N. J.

(Philadelphia Meeting, September, 1919)

ONE of the most useful, and at the same time least commonly used, methods of thermal analysis for the determination of transformations in metals and alloys consists in the recording of the time intervals required for successive increments of temperature change during heating or cooling, the temperature of the furnace containing the specimen being altered at a uniform rate. The curve obtained by plotting these time intervals as a function of the mean temperature of the specimen durnig the interval is called the inverse-rate curve. It is probably due to the fact that no simple and convenient method has apparently been available for the measurement of the successive time intervals that this method has not been so generally used as, for example, the differential method, for which several types of automatic or semi-automatic apparatus have been designed.

Whenever this method has been used, the intervals have usually been measured with the use of a chronograph; its operation as practised at the Bureau of Standards[1] is as follows: The temperature of the specimen is measured by a thermocouple and a dial potentiometer. The operator sets the potentiometer at successive values of the electromotive force differing by equal increments, usually 0.02 millivolt, and records the exact instant on the chronograph, by pressing a contact key, at which the galvanometer coil passes through its null position. Two-second intervals are also recorded on the chronograph record, and the number of seconds elapsing between successive signals is afterward counted from the record and plotted as a function of the electromotive force or of the temperature. This is an admirable method and by it most minute thermal arrests may be detected, but it requires a good chronograph, which is generally difficult to obtain, and the time of one operator during the recording and, subsequently, to read the intervals from the record; the latter operation often takes from one to two hours.

There is here suggested a simple, convenient, and, it is believed, equally accurate method of recording the successive time intervals, by which the

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* Published also as Bureau of Standards *Sci. Paper* 336 (1919).

† Physicist, U. S. Bureau of Standards.

[1] G. K. Burgess and J. J. Crowe: Critical Ranges, A_2 and A_3, of Pure Iron. Bureau of Standards, *Bull.* 213 (1914).

expense of chronograph and the time of one operator in counting the chronograph record may be eliminated. The remainder of the apparatus (consisting of furnace, thermocouple, and potentiometer) is used exactly as in the former method. Two stop watches are used, which may be mounted in a small frame and held in one hand, a finger being placed on each stem. During the "run," the operator sets the potentiometer and marks the instant at which the galvanometer is at zero by pressing the

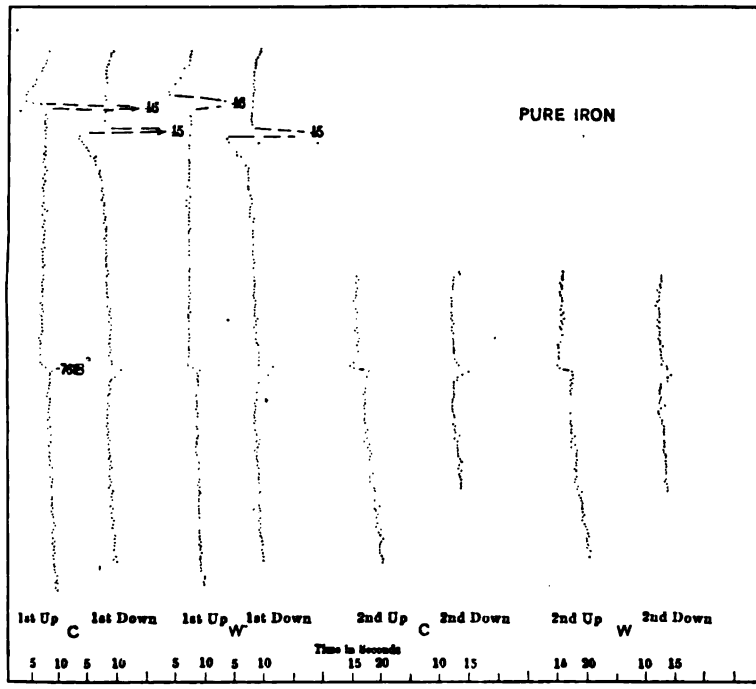

FIG. 1.—INVERSE-RATE HEATING AND COOLING CURVES OF PURE IRON TAKEN WITH CHRONOGRAPH (C) AND WITH STOP WATCHES (W). A_2 AND A_3 ARE SHOWN ON THE FIRST SET OF CURVES, ONLY A_2 ON THE SECOND SET.

stems of both watches simultaneously, stopping one at the end of the interval it has measured and starting the other upon its measurement of the next. The interval is read and recorded upon a suitable blank sheet, the hand of this watch returned to its zero position and the potentiometer set at the next value. The operation is repeated for each successive interval. The intervals so recorded are afterwards plotted directly as a function of the electromotive force.

Fig. 1 shows the inverse-rate curves for two complete "runs," including the heating and the cooling curve, made on pure iron. Both A_3 and A_2 are indicated on the first set of curves, but only A_2 on the second set. In each case, the intervals were recorded both with the

stop watches and with the chronograph in the usual manner; the curves marked *C* were taken with chronograph, those marked *W*, with stop watches. There is little difference in the smoothness of the two sets of curves or in the accuracy or precision of the measurement of the time interval.

A general consideration of the accuracy of the stop watch also indicates that the precision of measurement by stop watch is sufficient for the purposes of thermal analysis. It is only rarely, perhaps once in a hundred times, that a stop watch is not accurate to within $\frac{1}{5}$ sec., and its maximum error is $\frac{2}{5}$ sec. It is found that the variation of successive intervals of time measured in the inverse-rate method, due to actual non-uniform rate of cooling or heating of the furnace, or to inaccuracy of the operator in signaling the moment when the potentiometer is balanced, is of approximately the same value; *i.e.*, $\frac{1}{5}$ sec. It is therefore not necessary to obtain the greater precision of time measurement which is unquestionably possible by the use of the chronograph.

When the ordinary dial type of precision potentiometer is used, the operator has sufficient time for all of the operations necessary—setting the potentiometer, reading, and recording the time interval from the watch—within an average interval of 15 sec., which is recommended for usual conditions.

The curves recorded were taken with a stop watch costing about $10. It does not appear that a more expensive watch is necessary; however, it is not advisable to use a stop watch that also has the hour and second hands, as the presence of so many hands will only confuse the operator, who is obliged to read quickly and cannot take much time in recognizing the stop hand.

The author acknowledges the assistance of Miss H. G. Movius in obtaining the curves here shown.

Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, Nickel, and Manganese*

BY P. D. MERICA,† PH. D.; R. G. WALTENBERG,‡ B. S.; AND A. N. FINN,§ M. A., WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

CONTENTS

PAGE

Introduction 29
Preparation of Alloys 30
Composition of Alloys 32
Mechanical Tests 34
Corrosion Tests 36
Summary 39

INTRODUCTION

CERTAIN compositions of the light, *i.e.*, aluminum-rich, alloys of aluminum with magnesium and copper have become quite well known within the past ten years under the name of duralumin. These alloys are used for rolling and forging and can be so treated as to develop quite remarkable mechanical properties. Thus a properly heat-treated alloy containing about 4 per cent. of copper and about 0.5 per cent. of magnesium, rolled into sheet or rod, will have a tensile strength of approximately 55,000 lb. per sq. in. (3866 kg. per sq. cm.) with an elongation in 2 in. (50.8 mm.) of about 15 per cent. This alloy, duralumin, was developed by Wilm,[1] and its properties more fully described by Cohn.[2]

The authors considered it worth while to investigate the mechanical possibilities of the light alloys of two somewhat analogous ternary series; namely, of aluminum-magnesium-nickel and aluminum-magnesium-manganese, to study the effect of variation of composition upon mechanical properties within the alumimum-rich group of the aluminum-magne-

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* Published also as Bureau of Standards *Tech. Paper* 132 (1919).

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§ Associate Chemist, U. S. Bureau of Standards.

[1] A. Wilm: *Metallurgie* (1911) **8**, 225, 650.

[2] L. M. Cohn: *Zeit. z. Beförderung d. Gewerbefleisses* (1910) **89**, 643; also in *Electrotechnik u. Maschinenbau* (1912) **30**, 809, 829.

sium-copper alloys and to compare the mechanical properties of the three ternary series.

This work was carried out with the coöperation of the Aluminum Company of America; the alloys were prepared there and most of the mechanical tests were performed by Mr. Waltenberg in the laboratories of the company at New Kensington. The authors wish to express their appreciation of the aid and assistance thus given by the company through Mr. E. Blough.

No previous investigation has been made, or at least published, of these three ternary systems, except that dealing with the compositions called duralumin mentioned above. Light alloys of other related alloy series have been prepared and their properties investigated; viz., those of aluminum-copper,[3] aluminum-manganese,[4] aluminum-nickel,[4,5] aluminum-magnesium,[4] aluminum-manganese-copper,[6] and aluminum-nickel-copper.[5]

Preparation of Alloys

The alloys were prepared by melting standard 99 per cent. aluminum ingots with the proper amount of aluminum hardener, consisting of an alloy of aluminum and the magnesium, copper, nickel, or manganese depending on the alloy to be produced. The melts were made in crucibles, attention being given to see that the temperature during melting did not exceed 800° C., as above this temperature the ingots poured from crucibles are apt to be porous and unsound, due to the absorption of gas by the metal. The melting temperature was usually about 700° C. The molten metal was poured into water-cooled iron molds giving ingots 3.5 by 12 by 24 in. (9 by 30 by 60 cm.) in dimensions.

These ingots were reheated to from 400° to 450° C. in a large reheating furnace, sent to the hot rolls, rolled and cross-rolled at these temperatures to a thickness of 0.25 in. (6.35 mm.). They were then allowed to cool in the air and cold-rolled to 0.081 in. (2.05 mm.) thickness (No. 12 B. & S.), annealed at from 400° to 450° C., rolled-cold to 0.051 in. (1.29 mm.) thickness (No. 16 B. & S.), annealed again and finished cold at 0.032 in. (0.8 mm.) thickness (No. 20 B. & S.).

Test specimens prepared from these sheets were tested in the cold-rolled condition, after annealing at 422° C., and after heat treatment, consisting of quenching at various temperatures and allowing the quenched

[3] H. C. H. Carpenter and C. A. Edwards: *Proc.* Inst. Mech. Eng. (1907) 57.
[4] H. Schirmeister: *Stahl u. Eisen* (1915) **35**, 648, 873.
[5] A. A. Read and R. H. Greaves: *Jnl,* Inst. Met. (1915) **13**, 100.
[6] W. Rosenhain and F. C. Lantsberry: *Proc.* Inst. Mech. Eng. (1910), 119.

TABLE 1.—*Composition of Alloys**

Number of Sample	Chemical Composition						
	Aluminum, Per Cent.	Magnesium, Per Cent.	Copper, Per Cent.	Manganese, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.
B-1	97.00	1.15	0.02	1.04	None	0.48	0.31
B-2	97.17	None	0.04	1.71	None	0.76	0.32
B-3	96.14	1.09	0.15	1.68	None	0.56	0.38
B-4	98.02	None	0.08	1.07	None	0.44	0.39
B-5	95.08	2.03	0.08	1.68	None	0.76	0.37
B-6	96.86	1.44	0.10	0.93	None	0.40	0.27
B-7	96.31	1.99	0.03	0.94	None	0.41	0.32
C-1	97.27	1.16	0.72	None	None	0.56	0.29
C-2	96.69	2.37	0.04	None	None	0.62	0.28
C-3	97.15	None	2.15	None	None	0.36	0.34
C-4	96.65	2.84	0.04	None	None	0.27	0.20
C-5	96.11	None	3.19	None	None	0.40	0.30
C-6	96.72	2.03	0.72	None	None	0.30	0.23
C-7	96.62	1.00	1.80	None	None	0.35	0.23
C-8	96.68	1.07	1.67	0.02	None	0.33	0.23
C-9	95.98	3.50	0.08	None	None	0.26	0.18
C-10	95.83	2.95	0.74	None	None	0.27	0.21
C-11	95.51	1.26	2.58	0.02	None	0.41	0.22
C-12	95.74	0.46	3.18	None	None	0.34	0.24
A-1-12	95.48	0.64	3.22	None	None	0.39	0.27
E-3	96.80	1.06	1.56	None	None	0.32	0.26
D-1	97.44	0.98	0.02	None	1.00	0.36	0.20
D-2	97.47	None	0.08	None	1.76	0.44	0.25
D-3	95.82	None	0.02	None	3.40	0.44	0.32
D-4	96.04	1.18	0.08	None	1.98	0.48	0.24
D-5	96.70	1.84	0.06	None	0.80	0.43	0.17
D-6	95.62	1.94	0.04	None	1.80	0.46	0.14
D-7	95.14	None	0.06	None	3.94	0.58	0.28
D-8	94.65	0.94	0.09	None	3.54	0.65	0.13
D-9	95.41	2.86	0.06	None	1.08	0.39	0.20

* Aluminum determined by difference.

specimens to stand, or "age," for several days before testing. The latter feature of this heat treatment will henceforth be termed "aging," and is necessary in order to develop the highest mechanical properties in the light alloys of the aluminum-copper-magnesium series. It will be noticed that some of the alloys of the latter series were aged at 110° C. whereas the others were aged only at about room temperature (20° C.).

TABLE 2.—*Mechanical Properties of Alloys of Aluminum-Magnesium-Manganese*

No. of Sample	As Rolled			Annealed at 371° C.			Annealed at 422° C.			Quenched from 500° C. Aged 8 days at 20° C.		
	Scleroscope Hardness[a].	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation in 2 In. Per Cent.	Scleroscope Hardness[a].	Ultimate Tensile Strength, Lb. Per Sq. In.	Elongation in 2 In. Per Cent.	Scleroscope Hardness[a].	Ultimate Tensile Strength, Lb. Per Sq. In.	Elongation in 2 In. Per Cent.	Scleroscope Hardness[a].	Ultimate Tensile Strength, Lb. Per Sq. In.	Elongation in 2 In. Per Cent.
B-1	30.0	32,400	2.0	13.5	25,500	14.0	11.5	24,700		12.0	22,300	22.0
		31,600	2.0		25,300			24,700	13.0		23,100	25.0
		32,400	2.5		25,900	19.0		23,400	11.5		22,900	17.0
		31,000	2.0									
B-2	20.0	24,000	4.5	10.5	16,800	26.0	8.5	16,000	30.5	8.5	14,200	36.5
		22,000	3.5		16,700	24.0		16,000	35.5		14,600	36.5
		24,100	4.0		16,200	31.0		15,800	30.0		14,400	35.0
B-3	32.0	34,600	2.0				14.0	26,400		14.0	25,300	18.0
		35,000	2.0					26,000	14.0		24,700	17.5
		35,600	2.5					25,800	12.0		24,900	20.0
B-4	20.0	21,500					6.5	14,300	42.0	7.0	12,800	26.0
		22,500	3.0					13,700	41.0		12,900	40.0
		22,100	3.0					13,300	41.0		12,300	35.0
		23,500	3.0									
		22,900	3.0									
		22,300	5.5									
		23,500	4.0									
B-5	36.0	39,300	2.0				13.5	29,400	20.0	15.0	28,800	16.0
		40,300	2.0					28,600	16.0		29,400	15.0
		37,500	2.0					28,600			28,000	
B-6	36.5	45,000	3.5				14.0	33,100	13.0	15.5	34,100	19.0
		42,700	2.5								33,100	17.0
											32,600	17.0
B-7	35.5	37,200	2.5				13.0	29,600	15.5	14.0	29,000	19.5
		40,700	4.0					29,200	17.0		29,000	19.5
											29,400	18.0

[a] Taken with magnifying hammer.

COMPOSITION OF ALLOYS

It was desired to include in the list of alloys that were to be prepared compositions of each ternary series with the individual percentages of the components varying by intervals of 1 per cent. and with a total combined content of hardening components not exceeding 4.5 per cent., since with a smaller aluminum content these alloys cannot be readily rolled into sheets. The actual compositions obtained, as determined by chemical analysis, are given in Table 1. The B series is that containing manganese, the C series that containing copper, and the D series that containing nickel.

TABLE 3.—*Mechanical Properties of Alloys of Aluminum-Magnesium-Copper*

	As Rolled			Annealed at 422° C.			Quenched from 510° C.		
Number of Sample	Sclero-scope Hard-ness[a]	Ultimate Tensile Strength, Lb. Per Sq. In.	Elonga-tion in 2 In., Per Cent.	Sclero-scope Hard-ness[a]	Ultimate Tensile Strength, Lb. Per Sq. In.	Elonga-tion in 2 In., Per Cent.	Sclero-scope Hard-ness[a]	Ultimate Tensile Strength, Lb. Per Sq. In.	Elonga-tion in 2 In., Per Cent.
C-1	42	49,000	2.0	15.5	33,300		17.0	38,030[b]	17.0
		48,400	2.5		33,100	15.0		37,220[b]	16.5
		48,600	2.5		32,700	14.0	27.0	48,120[c]	16.0
		49,600	2.5					47,210[c]	18.5
C-2	19	25,800	4.0	7.5	16,600	35.0	8.0	16,670[b]	34.0
		23,600	3.0		15,900	35.0		16,670[b]	33.0
		23,600	3.5		16,100	33.0		16,510[c]	28.0
								16,510[c]	33.0
C-3	35	34,900	2.5	7.0	21,600	31.0	13.0	26,350[b]	19.0
		35,700			21,800	33.0		27,690[b]	11.5
		34,000	1.5		22,000	33.5	11.0	29,420[c]	20.0
								27,790[c]	19.5
C-4	37	38,400		10.5	29,200	18.0	11.0	30,060[b]	23.0
		38,600	1.5		29,200	18.0		29,700[b]	16.5
		37,200	1.5		29,400	21.0	14.0	31,590[c]	19.0
								31,350[c]	20.0
C-5	34	35,900		8.0	23,000	30.0	14.0	31,960[b]	15.5
		37,500	2.5		22,400	28.5		30,500[b]	14.0
		37,700	2.0		22,800	32.5		30,910[c]	19.0
								33,970[c]	
C-6	38	35,300	1.0	13.0	30,500		15.0	33,370[b]	17.0
		38,500	0.5		29,900	18.5		33,950[b]	23.5
		38,100	1.5		30,800	16.0	26.0	43,190[c]	18.5
								43,560[c]	18.0
C-7	44	44,200	2.0	17.0	35,300	26.0	24.0	45,650[b]	18.5
		45,500	2.0		34,600	25.5		45,740[b]	19.5
		45,300			34,800	25.0	35.0	53,970[c]	20.0
								52,250[c]	
C-8	38	38,100	1.5	12.5	28,500	18.5			
		38,100			29,100	18.5			
C-9	38	41,200	1.5	12.0	31,600	17.5	13.0	29,120[b]	21.0
		43,200	1.5		31,200	17.5		29,500[b]	22.0
		41,200	1.5		30,500		14.0	30,270[c]	23.0
								30,270[c]	22.0
C-10	45	44,800	1.5	12.0	30,600	19.0	14.0	37,430[b]	24.5
		44,600	1.5		30,200	19.0		37,630[b]	21.5
		47,500	1.5		30,200	17.0	26.0	47,690[c]	21.5
								47,690[c]	22.5
C-11	50	56,700	2.0	15.5	34,900	20.5	29.5	51,520[b]	21.0
		52,900	1.5		36,000	24.0		50,870[b]	24.0
		58,400	2.0				34.0	54,740[c]	23.0
								55,590[c]	20.0
C-12	31	38,900	5.0	7.5	23,100	24.0	25–28	42,370[b]	14.5
		38,600	5.0		23,000	24.0		39,340[b]	16.5
							26	49,230[c]	26.5
								49,830[c]	25.5

[a] Taken with magnifying hammer. [b] Aged at 20° C. [c] Aged at 110° C.

Mechanical Tests

The results of the tests made on the strips cut from the sheets are given in Tables 2, 3, and 4.

Table 4.—*Mechanical Properties of Alloys of Aluminum-Magnesium-Nickel*

No. of Sample	As Rolled				Annealed at 500° C.			Quenched from 500° C. Aged 20 Days at 20° C.		
	Sclero-scope Hard-ness*	Ultimate Tensile Strength, Lb. Per Sq. In.	Yield Point, Lb. Per Sq. In.	Elonga-tion in 2 In., Per Cent.	Sclero-scope Hard-ness*	Ultimate Tensile Strength, Lb. Per Sq. In.	Elonga-tion in 2 In., Per Cent.	Sclero-scope Hard-ness*	Ultimate Tensile Strength, Lb. Per Sq. In.	Elonga-tion in 2 In., Per Cent.
D-1	23.0	23,800		3.0	7.0	17,800	15.0	15.0	27,700	18.0
		25,500	21,000	3.5	7.0	17,900	18.5	14.0	26,200	21.0
D-2	22.0	24,900	17,500	2.5	7.0	18,000	29.5	7.5	18,600	28.5
		25,200	18,000	2.5	6.5	17,700	24.0	7.0	18,600	27.0
D-3	27.0	32,100		3.0	8.0	21,600	27.0	10.0	21,600	24.0
		32,600		3.5	8.0	20,600	29.0	9.0	21,600	20.0
D-4	27.5	29,900	25,500	2.0	9.5	20,900	20.0	13.0	27,900	18.0
		29,300	25,500	2.5	9.5	21,100	20.5	14.0	27,100	17.0
D-5	29.0	33,000	30,000	4.0	10.0	24,200	21.0	12.0	28,100	19.0
		34,300	29,000	4.5	11.0	21,100	16.5	12.5	27,600	18.5
D-6	30.0	36,900	31,000	1.5	11.0	25,200	18.0	14.0	29,900	20.0
		35,200	31,000	1.0	12.0	25,400	18.5	13.5	29,100	21.5
D-7	24.0	29,200	21,000	3.0	10.0	20,200	23.0	9.0	22,700	21.5
		29,300	21,000	3.0	10.0	20,200	24.5	10.0	22,400	21.5
D-8	28.0	33,800	28,500	2.5	10.5	21,400	19.0	16.0	31,000	15.0
		34,100	29,000	1.5	11.0	22,600	19.0	15.0	31,500	15.0
D-9	32.0	42,000	35,000	3.0	13.0	28,900		14.0	32,200	18.0
		40,600	34,500	3.0	13.5	28,800		15.0	31,800	16.0

* Taken with magnifying hammer.

The alloys of aluminum-manganese and of aluminum-manganese-magnesium are not improved by heat treatment of the type used for duralumin. The alloys of aluminum-nickel alone are also not appreciably affected by this heat treatment (See Nos. D-2, D-3, and D-7), but in those alloys in which both nickel and magnesium are present the heat-treated specimens are harder and stronger than the annealed ones.

Within the C series, it is noticed that alloys containing magnesium but no copper are not improved by heat treatment; alloys containing copper but no magnesium are moderately affected; the greatest increases in hardness and strength are found in the heat-treated specimens of alloys containing both copper and magnesium. Table 5 gives a survey of the percentage increase of strength of the heat-treated over the annealed specimens of the same composition.

TABLE 5.—*Percentage Increase of Tensile Strength of Heat-treated Specimens over Annealed Ones of Same Composition*

Alloys Containing	Average Increase, Per Cent.
Manganese, no magnesium, B-2 (− 9 per cent.), B-4 (− 7 per cent.)	−8
Manganese and magnesium, B-1 (− 4 per cent.), B-3 (−5 per cent.), B-5 (0), B-6 (0), B-7 (−2 per cent.)	−3
Nickel, no magnesium, D-2 (3 per cent.), D-3 (3 per cent.), D-7 (12 per cent.)	6
Nickel and magnesium, D-1 (40 per cent.), D-4 (31 per cent.), D-5 (24 per cent.), D-6 (17 per cent.), D-8 (41 per cent.), D-9 (11 per cent.)	27
Copper, no magnesium, C-3 (28 per cent.), C-5 (41 per cent.)	34
Magnesium, no copper, C-2 (3 per cent.), C-4 (10 per cent.), C-9 (− 3 per cent.)	3
Copper and magnesium, C-1 (44 per cent.), C-6 (43 per cent.), C-7 (50 per cent.), C-10 (58 per cent.), C-11 (57 per cent.), C-12 (110 per cent.)	60

TABLE 6.—*Comparison of Hardening or Strengthening Effect of Copper, Nickel, Manganese, and Magnesium on Annealed Specimens*

Number	Alloying Elements	Tensile Strength, Lb. Per Sq. In.	Elongation, Per Cent.
C-3	Cu 2.15	21,800	32
B-2	Mn 1.71	16,000	32
D-2	Ni 1.76	17,800	27
C-2	Mg 2.37	16,000	35
C-5	Cu 3.19	22,800	30
D-3	Ni 3.40	21,100	28
C-4	Mg 2.84	29,000	19
C-1	Cu 1.16, Mg 0.72	33,000	15
B-1	Mn 1.04, Mg 1.15	24,000	12
D-1	Ni 1.00, Mg 0.98	17,700	17
C-7	Cu 1.80, Mg 1.00	35,000	25
B-3	Mn 1.68, Mg 1.09	26,000	13
D-4	Ni 1.98, Mg 1.18	21,000	20
C-6	Cu 0.72, Mg 2.03	30,000	17
B-5	Mn 1.68, Mg 2.03	29,000	18
D-6	Ni 1.94, Mg 1.94	25,000	18

In the annealed condition and for equal additions, either with or without magnesium, copper seems to confer the greatest hardening effect, next manganese, and then nickel. This is shown in the comparisons of Table 6.

At about 3 per cent., magnesium alone appears to exert a greater hardening effect than the same percentage of the other metals but at about 2 per cent. it has less effect than copper.

Corrosion Test

The resistance of these alloys to corrosion was determined by the salt-spray test. This test consists of exposing the samples to a continuous fog of salt water, produced by atomizing a 20-per cent. solution of salt (sodium chloride) in water.[7] Although this test is not considered entirely satisfactory, it is thought that the results produced represent with a fair degree of accuracy the results obtained in actual service, especially under marine conditions.

The alloys were subjected to the salt-spray test for two periods of one month each, and were examined at the end of each period to deter-

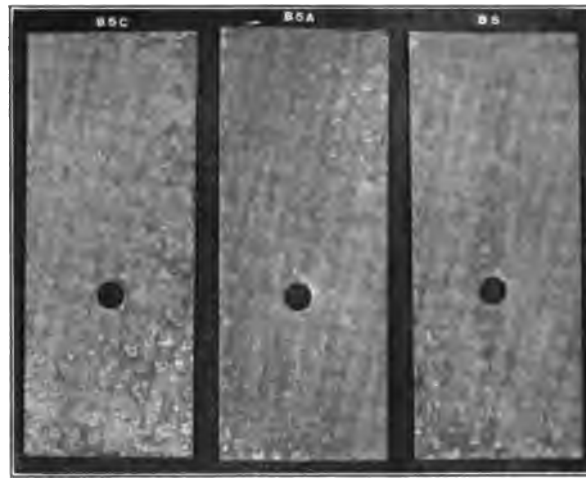

Fig. 1.—Photograph showing appearance of specimens of Al-Mg-Mn series after one month's exposure to action of salt spray.

mine the relative amount of corrosion. This was estimated by appearance only, as it is practically impossible to determine it by loss in weight on account of the adherence of the aluminum rust and the lack of a satisfactory reagent to remove the rust without affecting the metallic aluminum.

The test pieces were 4 by 2 by 0.03 in. (101 by 50.8 by 0.76 mm.) and included each series of alloys treated as follows: as rolled (marked B-4, etc.), quenched from 520° C. into water at 16° C. (marked B-4-A, etc.), quenched from 520° C. into water at 100° C. (C-2-B, etc.), annealed at 450° C. and cooled slowly (B-4-C, etc.). Specimens of commercial sheet aluminum, as rolled marked (A1), annealed at 450° C. (A1-A), annealed at 500° C. (A1-B), and quenched from 500° C. (A1-C) were tested in the same way.

[7] A. N. Finn: Method of Making Salt-spray Test. *Proc.* Am. Soc. Test. Mat. (1918) **18**, pt. 1, 237.

After one month's exposure to the salt spray, there was a marked difference in the appearance of the various rolled alloys. B-4 and B-5 as rolled, annealed, and quenched were only slightly corroded and appeared better than the remaining alloys. The annealed specimens, B-4-C and

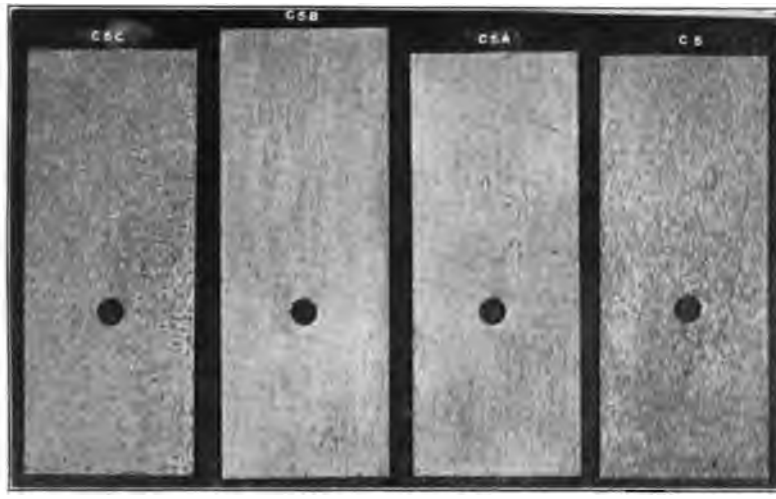

FIG. 2.—PHOTOGRAPH SHOWING APPEARANCE OF SPECIMENS OF AL-MG-CU SERIES AFTER ONE MONTH'S EXPOSURE TO ACTION OF SALT SPRAY.

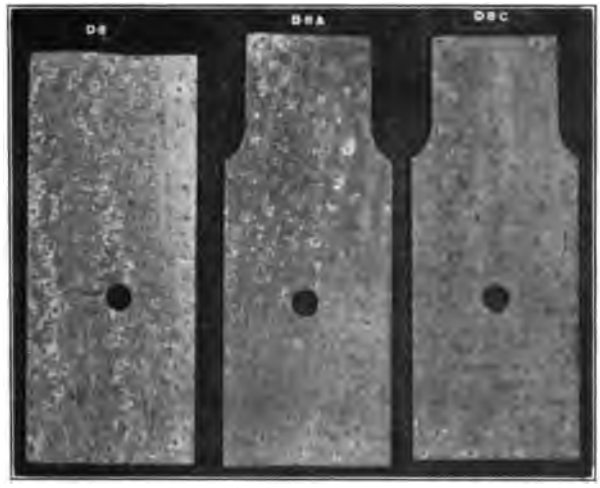

FIG. 3.—PHOTOGRAPH SHOWING APPEARANCE OF SPECIMENS OF AL-MG-NI SERIES AFTER ONE MONTH'S EXPOSURE TO ACTION OF SALT SPRAY.

B-5-C, were corroded more than the rolled or the quenched specimens of these alloys. Specimens of D-3, D-6, and D-8, rolled, annealed, and quenched were not quite as good as the B series. The specimens as rolled were corroded a little more than the annealed or quenched specimens.

The rolled specimens of the C series (C-2, C-5, C-8, etc.), with the exception of C-2, were badly corroded. C-2, as rolled, annealed, and quenched, C-11 annealed and quenched, and the quenched specimens of the remainder of this series compared favorably with B-4 and B-5.

Figs. 1, 2, and 3 show the appearance of some of the specimens after one month's exposure.

In Table 7 the alloys are grouped according to their resistance to corrosion, as indicated by their appearance at the end of the second month, group I being the most resistant and group IV the least resistant.

TABLE 7.—*Arrangement of Specimen in Order of Resistance to Corrosion*

Group I	Group II	Group III		Group IV
B-5-A	C-11-B	B-5-C	C-11-C	C-11
B-4-A	C-11-A	B-4-C	C-2	C-8
B-5	C-5-B	B-4	C-8-C	C-5
C-8-B	C-5-A	C-2-B	D-3-A	C-12
C-8-A	C-12-A	D-6-C	C-2-C	C-5-C
	C-12-B	D-6-A	C-2-A	C-12-C
		D-6	D-3	A1
		A1-A	D-8	
		A1-B	D-3-C	
		A1-C	D-8-A	
			D-8-C	

It must be stated that there was not the distinct difference in the amount of corrosion that might be inferred from the above classification, but the difference was very small or negligible between pieces in the same group; group I merges with group II, but the difference between groups II and III, and between III and IV is very definite.

The order in which the thirty-nine samples listed above are grouped is based on the opinion of two observers working independently of each other, and it is notewothy that the results of their observations were in almost complete agreement. In no case was any sample placed by either observer in a different group from that indicated above, and in only a few cases did the indicated order differ.

Table 8 gives, in condensed form, a summary of the corrosion tests and shows at a glance the relative resistance to corrosion of the alloys studied and the effect produced by quenching and annealing the rolled alloys. The figures indicate the group in which a particular alloy was classed with respect to its resistance to corrosion. Consideration of this table indicates clearly that a decided increase in resistance to corrosion may be produced by quenching some aluminum alloys, a less marked difference is produced by annealing, and with some alloys no difference is noted.

The following conclusions are drawn from examination of this table: if any change is produced by quenching, it improves the resistance of the metal to corrosion; the magnesium, nickel, and nickel-magnesium alloys have about the same resistance to corrosion regardless of treatment; annealing improves somewhat the resistance to corrosion of the copper-

TABLE 8.—*Relative Corrosion*

Treatment	Alloying Metals	B-4	B-5	C-2	C-5	C-8, C-11, C-12	D-3	D-6, D-8	A1
		Mn	Mn–Mg	Mg	Cu	Cu–Mg	Ni	Ni–Mg	
	As rolled.....	3	1	3	4	4	3	3	4
	Quenched 520° to 16° C. (A).....	1	1	3	2	1 and 2	3	3	3
	Quenched 520° to 100° C. (B)....	*	*	3	2	1 and 2	*	*	*
	Annealed at 450° C. (C).....	3	3	3	4	3 and 4	3	3	3

*No samples tested.

magnesium alloys and reduces the resistance of the manganese-magnesium alloy; quenching produces the greatest effects in the copper, copper-magnesium, and manganese alloys; commercial aluminum, as hard rolled, does not resist corrosion satisfactorily and the sample tested was almost completely disintegrated at the end of the test showing characteristic exfoliation. Annealing or quenching materially improves aluminum, but it is not equal to some of the alloys.

SUMMARY

Light aluminum alloys of several compositions belonging to each of the three ternary series, aluminum-magnesium-copper, aluminum-magnesium-manganese, and aluminum-magnesium-nickel were rolled out into sheets and tested in tension as cold-rolled, after annealing, and after heat treatment, consisting of quenching from about 500° C. and aging at ordinary temperature.

The tensile properties of the alloys of the aluminum-magnesium-copper series were superior in all conditions to those of the other series. They may be much improved by an appropriate heat treatment. The alloys of the aluminum-magnesium-nickel series are also improved by heat treatment, but not in the same degree as the former series. The alloys of the aluminum-magnesium-manganese series are not improved by heat treatment.

Samples of representative compositions of each series were exposed to corrosion in the salt-spray test, and the appearance of the samples observed after exposure to the action of the salt spray for one and for two months. The alloys of the aluminum-magnesium-manganese series resisted corrosion, in general, better than those of the other series; this observation agrees with other experience in the corrosion of such alloys. The heat-treated specimens of the aluminum-magnesium-copper series, however, were but little inferior to those of the manganese series in their resistance to corrosion; the annealed and the cold-rolled samples of that series were the least resistant to corrosion of any of the alloys tested. Hard-rolled commercial aluminum corroded much more than any of the alloys. Annealed aluminum was more resistant to corrosion than the hard-rolled aluminum, but did not compare favorably with most of the alloys.

DISCUSSION

G. K. BURGESS,* Washington, D. C.—In the service tests, the Advisory Committee on Aeronautics considered it highly necessary, particularly for seaplanes, to find out whether or not it was necessary to paint exposed parts; reports have been obtained but have not been published at the present time. Investigations were carried on at three Navy Yards. On just a hurried examination, the inspection was made about two weeks ago and the results are now being digested—an examination shows that the aluminum alloys, whether painted or unpainted, stand up very well. It apparently is not necessary to paint, which, of course, is a very important item in the question of the weight of seaplanes. We will be able to report on that, I expect, probably at the next meeting.

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Heat Treatment and Constitution of Duralumin*

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WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

CONTENTS

	PAGE
Introduction	41
Composition and Preparation of Alloys	43
Heat Treatment and Aging	43
Effect of Quenching Temperature	47
Effect of Aging Temperature	50
Effect of Temperature of Quenching Bath	53
Effect of Prior Heating at Quenching Temperature	53
Effect of Preheating to 515° C. before Quenching from Lower Temperature	54
Miscellaneous Tests	54
Density and Dilatation	55
Electrical Resistivity	59
Mechanism of Hardening During Aging after Rapid Cooling	61
Structure of Duralumin	65
Analogy Between Hardening of Duralumin and that of Steel	71
Eutectic Structure and Influence of Magnesium	72
Conclusions Relative to Manufacture and Heat Treatment of Duralumin	75
Summary and Conclusions	76

INTRODUCTION

The remarkable phenomena exhibited by the aluminum alloy known as duralumin were discovered during the years 1903–1911 by A. Wilm[1,2] and have been described by him and by others.[3,4,5,6]

The unusual feature of this alloy is the fact, as was shown by Wilm, that it can be hardened quite appreciably by quenching from tempera-

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* Published also as Bureau of Standards *Sci. Paper* 347 (1919).

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[1] A. Wilm: *Metallurgie* (1911) **8**, 225.

[2] A. Wilm: *Metallurgie* (1911) **8**, 650.

[3] L. M. Cohn: *Verh. Z. Befordering des Gewerbefleisses* (1910) **89**, 643.

[4] L. M. Cohn: *Elektrotechnik u. Maschinenbau* (1914) **31**, 430.

[5] L. M. Cohn: *Elektrotechnik u. Maschinenbau* (1912) **30**, 809, 829.

[6] P. D. Merica: Aluminum and its light alloys, *Circular* 76, U. S. Bureau of Standards, 1918; also *Chem. and Met. Eng.* (1918) **19**, 135, 200, 329, 587, 635, 729, 780.

tures below its melting point followed by aging at ordinary temperatures, which consists merely of allowing the material to stand at these temperatures. The hardness is not produced by the quenching alone but increases during the period of aging, which may be from one to three days. Cohn[3,5] gives data showing the increase of hardness of duralumin during aging, after quenching in water from about 450° C. Upon annealing, the alloy so hardened by aging is softened exactly as is hardened steel.

The composition of this alloy usually varies within the following limits: Copper, 3 to 4.5 per cent.; magnesium, 0.4 to 1.0 per cent.; manganese, 0 to 0.7 per cent.; aluminum, balance; iron (as impurities), 0.4 to 1 per cent.; silicon, 0.3 to 0.6 per cent. Its density is about 2.85. It is used only in the forged or rolled condition.

This alloy has been produced for some years commercially and is in demand for the fabrication of parts for which both lightness and strength are required, such as for aircraft. Its tensile strength will average 50,000 to 60,000 lb. per sq. in. (3515 to 4218 kg. per sq. cm.) after appropriate heat treatment, such as that described by Wilm.

With the purpose of ascertaining whether the heat treatment described by him actually developed the best mechanical properties possible for duralumin, the authors undertook a study of the effect of variation in heat-treatment conditions, *i.e.*, quenching temperature, aging temperature, etc., upon these properties and, in connection with another investigation,[7] a study of the effect of chemical composition upon them.

Mr. E. Blough had already called the attention of one of the authors to the fact that the amount of hardening produced by heat treatment was influenced quite markedly by the temperature from which the material was quenched, a most interesting fact that was not brought out by Wilm's published investigations, which mentioned merely the effect of aging after quenching from one temperature, in the neighborhood of 450° C. An explanation was sought for the mechanism of hardening during aging of this alloy, and additional data were obtained bearing upon this phase of the matter.

The experiments here described were carried out partly in the laboratories of the Bureau of Standards and partly in coöperation with The Aluminum Company of America in its laboratories at New Kensington. The alloys used were prepared at the New Kensington plant of this company and the authors wish to express their appreciation of the

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[7] P. D. Merica, R. G. Waltenberg and A. N. Finn: The Tensile Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, with Nickel and with Manganese. *Tech. Paper* No. 132, U. S. Bureau of Standards, 1919. Also this volume, p. 29.

assistance and coöperation which has been given throughout by this company through Mr. E. Blough, chief chemist. Mr. H. H. Beatty of Mr. Blough's staff was active in assisting this work.

Composition and Preparation of Alloys

In Table 1 are given the chemical compositions of the alloys of the aluminum-copper-magnesium series that were used in these experiments. The ingots, 12 by 24 by 3½ in. (30 by 60 by 8.89 cm.) were rolled hot, at about 410° C., to ¼ in. (6.35 mm.) thick and thereupon cold rolled to 0.081 in. (2.05 mm.) (12 B. & S. gage), annealed at about 425° C., rolled cold to 0.051 in. (1.29 mm.) (16 B. & S. gage), annealed again and cold rolled to 0.032 in. (0.81 mm.) (20 B. & S. gage). The casting and rolling were done at the New Kensington plant of the U. S. Aluminum Co.

Table 1.—*Composition of Alloys**

Number	Aluminum	Magnesium	Copper	Iron	Silicon
C-1	97.27	1.16	0.72	0.56	0.29
C-2	96.69	2.37	0.04	0.62	0.28
C-3	97.15	None	2.15	0.36	0.34
C-4	96.65	2.84	0.04	0.27	0.20
C-5	96.11	None	3.19	0.40	0.30
C-6	96.72	2.03	0.72	0.30	0.23
C-7	96.62	1.00	1.80	0.35	0.23
C-8	96.68	1.07	1.67	0.33	0.23
C-9	95.98	3.50	0.08	0.26	0.18
C-10	95.83	2.95	0.74	0.27	0.21
C-11	95.51	1.26	2.58	0.41	0.22
C-12	95.74	0.46	3.18	0.34	0.24
A-1-12	95.48	0.64	3.22	0.39	0.27
E-3	96.80	1.06	1.56	0.32	0.26
N-34	94.36	1.08	3.74	0.52	0.30
E-4	94.47	1.06	3.68	0.50	0.29

* Aluminum by difference.

Heat Treatment and Aging

Tensile tests and scleroscope measurements were made upon specimens taken from the sheets as rolled, from the rolled sheets annealed, and from the rolled sheets after heat treatment consisting of heating to various temperatures in a gas or electric furnace, quenching in water, and aging at room or other temperatures for different periods. The results of these tests are given in Table 2. All of the alloys, except those containing no copper (Nos. C-2, C-4, and C-9), show an increase of hardness of the heat-treated specimens over that of the annealed samples.

TABLE 2.—*Tensile Properties and Scleroscope Hardness of Rolled,*

No.	Tensile Properties and												
	As Rolled			After Annealing at 422° C.			After Heat Treatment Consisting						
							Quenched from 478° C.					Quenched	
							Aging, Days					Aging, Days	
	Scleroscope Hardness Magnifying Hammer	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness Magnifying Hammer	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	At 110°	At 20°	Scleroscope Hardness Magnifying Hammer	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	At 110°	At 20°
C-1	42	49,000	2.0	15.5	33,000			11		36,870	18.5		11
		48,400	2.5		33,100	15.0		11	20	37,080	17.0		11
		48,600	2.5		32,700	14.0		11		36,260	14.0	3	8
		49,600	2.5									3	8
C-2	19	25,800	4.0	7.5	16,600	35.0		11		16,830	35.0		11
		23,600	3.0		15,900	35.0		11	8	16,510	38.5		11
		23,600	3.5		16,100	33.0		11		16,510	38.5	3	8
												3	8
C-3	35	34,900	2.5	7.0	21,600	31.0		11		28,020	15.5		11
		35,700			21,800	33.0		11	11	25,810	25.0		11
		34,000	1.5		22,000	33.5		11		25,440	25.0	3	8
												3	8
C-4	37	38,400		10.5	29,200	18.0		11		29,300	20.0		11
		38,600	1.5		29,200	18.0		11	14	28,910	20.0		11
		37,200	1.5		29,400	21.0		11		30,280	22.0	3	8
												3	8
C-5	34	35,900		8.0	23,000	30.0		11		33,220	15.0		11
		37,500	2.5		22,400	28.5		11	15	32,580	18.5		11
		37,700	2.0		22,800	32.5		11		31,930	16.0	3	8
												3	8
C-6	38	35,300	1.0	13.0	30,500			11		31,050	20.0		11
		38,500	0.5		29,900	18.5		11	14	33,790	19.0		11
		38,100	1.5		30,800	16.0		11		31,640	17.5	3	8
												3	8
C-7	44	44,200	2.0	17.0	35,300	26.0		11		42,350	21.0		11
		45,500	2.0		34,600	25.5		11	23.5	42,530	21.0		11
		45,300			34,800	25.0		11		42,350	21.0	3	8
												3	8
C-8	38	38,100	1.5	12.5	28,500	18.5		13		46,400	19.5		11
		38,100			29,100	18.5		13	26	47,030			11
							7	6		48,900	20.0	3	8
							7	6	28.5	47,650	22.0	3	8
C-9	38	41,200	1.5	12.0	31,600	17.5		11		31,790	21.5		11
		43,200	1.5		31,200	17.5		11	15	30,450	18.0		11
		41,200	1.5		30,500			11		30,070	14.0	3	8
												3	8
C-10	45	44,800	1.5	12.0	30,600	19.0		11		38,030	26.0		11
		44,600	1.5		30,200	19.0		11	14	37,630	25.0		11
		47,500	1.5		30,200	17.0		11		38,430	22.5	3	8
												3	8
C-11	50	56,700	2.0	15.5	34,900	20.5		13		50,450			11
		52,900	1.5		36,000	24.0		13	28	48,950	22.0		11
		58,400	2.0				7	6		51,740	22.0	3	8
							7	6	31	50,880	22.0	3	8
C-12	31	38,900	5.0	7.5	23,100	24.0		11		38,330	14.0		11
		38,600	5.0		23,000	24.0		11	19–23	38,730	13.5		11
								11		35,910	12.5	3	8
												3	8

Annealed, and Heat-treated Aluminum-copper-magnesium Alloys

Scleroscope Hardness

of Quenching in Water and Aging

from 510° C.			Quenched from 520° C.					Quenched from 525° C.				
			Aging, Days					Aging, Days				
Scleroscope Hardness Magnifying Hammer	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	At 20°	At 110°	Scleroscope Hardness Magnifying Hammer	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	At 20°	At 110°	Scleroscope Hardness Magnifying Hammer	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
	38,030	17.0		11		36,870	18.5		11		37,220	14.0
	37,220	16.5		11	18.5	36,910	19.0		11	16	38,130	17.0
	48,120	16.0						3	8		50,140	17.0
27	47,210	18.5						3	8	27	49,930	17.5
	16,670	34.0		11		13,970	37.0		11		16,350	
8	16,670	33.0		11	8	14,290	35.0		11	8	16,870	35.0
	16,510	28.0						3	8		16,980	31.0
8	16,510	33.0						3	8	8	17,340	30.0
	26,350	19.0		11		24,700	18.5		11		28,550	23.0
13	27,690	11.5		11	13	25,440	21.0		11	13	28,640	
	29,420	20.0						3	8		26,800	17.5
11	27,790	19.5						3	8	10.5	26,980	20.0
	30,060	23.0		11		27,540	22.0		11		29,600	20.5
11	29,700	16.5		11	12	27,150	20.0		11	12	29,100	22.0
	31,590	19.0						3	8		34,850	17.0
14	31,350	20.0						3	8	17	35,350	16.5
	31,960	15.5		11		29,150	13.0		11		29,540	19.0
14	30,500	14.0		11	14	29,580	16.0		11	10.5	32,490	16.5
	30,910	19.0						3	8		28,170	23.0
14	33,970							3	8	12	27,960	26.0
	33,370	17.0		11		36,140	21.5		11		34,980	17.5
15	33,950	23.5		11	17	33,990	19.5		11	15	35,470	18.0
	43,190	18.5						3	8		47,580	20.5
26	43,560	18.0						3	8	26	45,840	16.5
	45,650	18.5		11		42,530	22.5		11		46,850	20.5
24	45,740	19.5		11	25	42,160	22.5		11	16	46,760	19.5
	53,970	20.0						3	8		54,170	21.0
35	52,250							3	8	35	56,110	19.0
	44,130	24.5		11		45,160	26.0		11		46,520	23.0
22	44,910	23.0		11	25.5	44,720	25.0		11	25	46,030	25.5
	49,680	19.5		11		44,720	21.0	3	8		53,440	21.0
32	51,530	17.0		11		44,070	22.0	3	8	31	53,000	19.0
	29,120	21.0		11		29,500	22.5		11		33,790	21.0
13	29,500	22.0		11	13	30,070	19.5		11	13	32,510	17.5
	30,270	23.0						3	8		34,800	17.5
14	30,270	22.0						3	8	18	34,890	18.0
	37,430	24.5		11		37,430	23		11		35,160	22.5
14	37,630	21.5		11	14.5	38,230	22		11	15	35,430	22.0
	47,690	21.5						3	8		44,260	19.9
26	47,690	22.5						3	8	26	46,450	20.0
	51,520	21.0										
29.5	50,870	24.0										
	54,740	23.0										
34	55,590	20.0										
	42,370	14.5							11		42,660	14.0
25–28	39,340	16.5							11	22	36,500	19.9
	49,230	26.5										
26	49,830	25.5						3	8	26	50,890	23.0

The increase of hardness in those alloys containing copper but no magnesium is smaller than that in those containing both, but is quite definite. This is shown in Table 3.

TABLE 3.—*Effect of Addition of Copper and Magnesium*

Number of Alloy	Increase of Tensile Strength of Heat-treated Alloy (510° C.) Over Annealed Alloy, Per Cent.	Number of Alloy	Increase of Tensile Strength of Heat-treated Alloy (510° C.) Over Annealed Alloy, Per Cent.
Alloys containing no copper		Alloys containing both copper and magnesium	
C-2	+ 2	C-1	45
C-4	+ 3	C-11	56
C-9	− 4	C-12	110
Alloys containing copper but no magnesium			
C-3	+30		
C-5	+36		

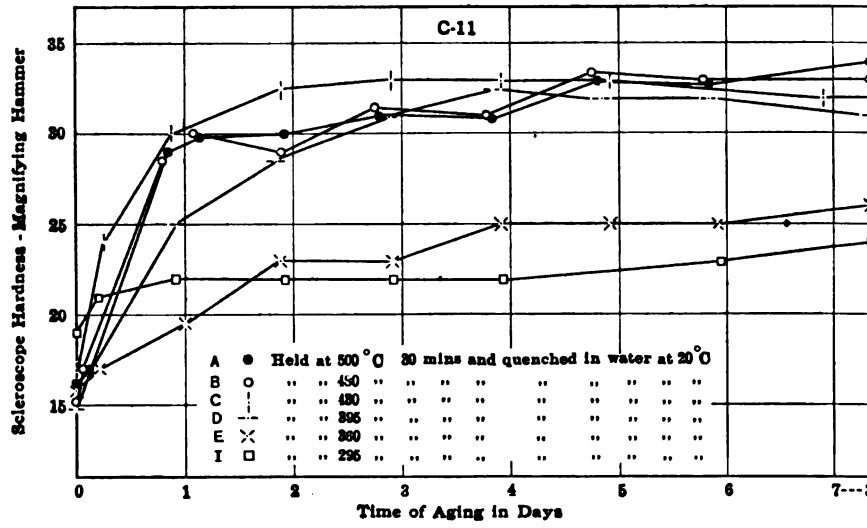

FIG. 1.—EFFECT OF QUENCHING TEMPERATURE ON SCLEROSCOPE HARDNESS DURING AGING OF QUENCHED SPECIMENS OF C-11.

The best mechanical properties are produced by quenching from the higher temperatures (500° to 525° C.). This is further shown in Table 4, which gives further data on two alloys, C-8 and C-11, and will be shown more clearly below. Not only does the hardness increase after heat treatment, but so does the ductility, as evidenced by the elongation in the tensile test. This is shown in Tables 2 and 4.

Effect of Quenching Temperature

In Fig. 1 are shown the scleroscope hardness values of C-11 quenched in water (20° C.) from different temperatures and aged at room temperature for periods of time from a few hours to 30 days. The form of these aging curves is similar to that shown by Cohn; *i.e.*, the hardness increases after quenching, at first rapidly and then more slowly. It is further evident that the maximum hardness attained increases with the temperature up to approximately 520° C.

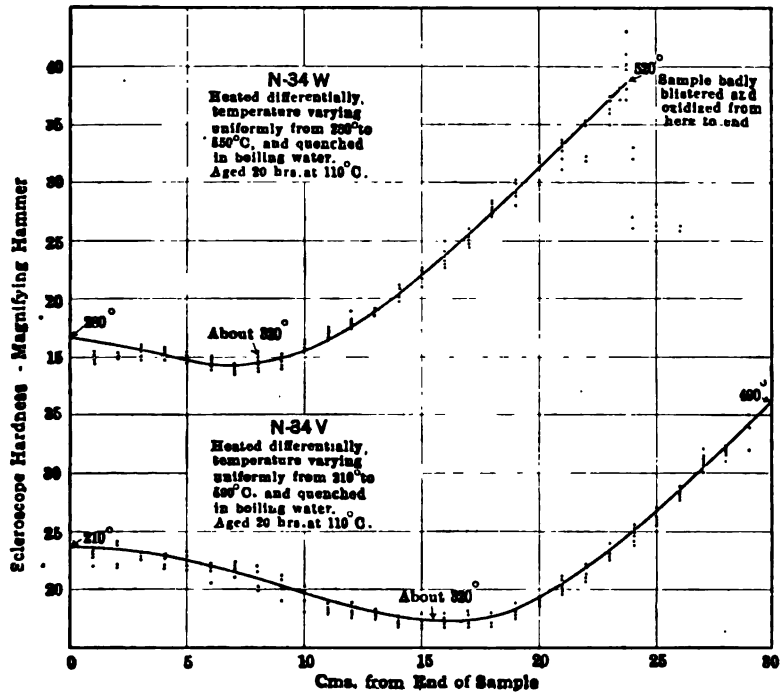

FIG. 2.—EFFECT OF QUENCHING TEMPERATURE ON SCLEROSCOPE HARDNESS. (ALLOY N-34.)

The effect of quenching temperature is also shown very nicely in an experiment of which the results are shown in Fig. 2. Two strips of 0.087-in. (2.20 mm.) sheet of alloy N-34 were used. The strip was placed in the furnace for heating in such a manner that a nearly linear temperature gradient existed between the two ends, as shown by thermocouples placed along the strip. Upon attaining the desired range of temperatures the strip was quenched in boiling water and aged 20 hr. at 110° C. The scleroscope hardness was then determined along the axis of the strip and is shown in Fig. 2 as a function of the distance from one end of the sample. The distance may be regarded as a rough temperature scale; the outside temperature limits have been determined and marked on the curve. One strip was quenched when the two ends were at 520°

TABLE 4.—*Effect of Quenching Temperature on Tensile Properties*

Temperature of Quenching, Degrees C.	Alloy C-8					Alloy C-11				
	Aging, Days		Mechanical Properties			Aging, Days		Mechanical Properties		
	At 20°	At 110°	Scleroscope Hardness	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	At 20°	At 110°	Scleroscope Hardness	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
371	13	..	..	27,260	16.0	13	..	..	35,900	19.0
	13		11	26,220	18.0	13	..	18	36,550	17.0
	7	6	..	29,130	18.5	7	6	..	35,020	21.0
	7	6	12	29,130	20.0	7	6	17	35,020	21.0
422	13	..	..	39,540	12.0	13	..	..	43,790	15.5
	13	..	23	40,160	13.5	13	..	25	43,360	18.5
	7	6	..	41,200	17.0	7	6	..	44,010	23.5
	7	6	23	41,200	22.0	7	6	24	43,580	24.0
478	13	..	..	46,400	19.5	13	..	..	50,450	
	13	..	26	47,030	....	13	..	28	48,950	22.0
	7	6	..	48,900	20.0	7	6	..	51,740	22.0
	7	6	28.5	47,650	22.0	7	6	31	50,880	22.0
500	11	..	..	47,230	18.5	11	..	..	52,590	20.5
	11	..	27	47,860	20.5	11	..	28	52,590	21.0
510	11	..	..	44,130	24.5	11	..	..	51,520	21.0
	11	..	22	44,910	23.0	11	..	29.5	50,870	24.0
	8	3	..	49,680	19.5	8	3	..	54,740	23.0
	8	3	32	51,530	17.0	8	3	34	55,590	20.0
520	11	..	..	45,160	26.0					
	11	..	25.5	44,720	25.0					
	11	..	..	44,720	21.0					
	11	..	..	44,070	22.0					
525	11	..	..	46,520	23.0					
	11	..	25	46,030	25.5					
	8	3	..	53,440	21.0					
	8	3	31	53,000	19.0					
533	13	..	..	34,960	5.0	13	..	..	48,370	9.5
	13	..	30–35	40,570	9.0	13	..	33	47,060	10.0

and 280° C., respectively; the other, when the ends were at 490° and 210° C., respectively. Beginning at about 300° C., the effect of increased quenching temperature, other factors remaining alike, is to increase the hardness after aging until a temperature of about 520° is reached.

TABLE 5.—*Effect of Temperature of Quenching Bath and Time of Aging in Quenching Bath*

(Specimen of Alloy A-1-12 Quenched from 520° C.)

Hours Aged in Quenching Bath Before Testing	Quenched to 20° C. Aged at 20° C.			Quenched to 100° C. Aged at 110° C.			Quenched to 150° C. Aged at 150° C.			Quenched to 200° C. Aged at 200° C.			Quenched to 230° C. Aged at 250° C.		
	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness
0	35,200	28.0	13.5	41,800	27.0	20.0	43,250	23.5	23	42,950	20.5	23	41,950	23.5	24
0	35,100	17.5	13.0	41,250	22.0	21.0	43,550	23.0	23	43,600	19.5	23	42,500	26.0	24.5
½	35,100	24.0	16.0				51,000	22.0	31	50,250	14.0	41	43,800		35
½							50,700	25.5	31	52,000	12.0	41	45,600	10.0	35
1	38,900	24.0	18.0	47,600	24.0	27.0	48,500	18.0	31	49,250	12.0	41–42	44,500		37
1	36,200	20.0	17.0	46,100	17.5	27	48,600	18.0	31	52,450	12.0	41–43	45,450	9.5	36
1½	36,000	20.0	20.0	47,500	21.5	25									
1½	38,200	22.5	19.0	49,500	24.0	26									
2	37,100	20.0	19.0	48,000	21.5	27	50,550	23.5	34	52,950	11.0	42	47,600	9.0	37
2	37,500	20.0	21.0	48,100	24.0	27	52,000	23.5	34	51,600	11.0	42	47,700	9.0	38
3							48,500	18.0	31	51,950	10.0	45–6			
3							49,450	18.0	31	54,250	10.0	44–5			
19	47,525	25.0	27.0	51,500	21.5	30									
19	47,450	18.0	28.0	52,250	26.0	32									
48	48,150	18.5	30.0	51,600	22.5	30									
48	49,050	22.0	30.0	52,750	20.5	32									
96	50,050	22.5	31.0												
96	50,300	22.5	31.0												

TABLE 6.—*Effect of Quenching in Baths at Different Temperatures Followed by Aging at Room Temperature (20° C.)*

(Specimen of Alloy A-1-12, Quenched to Room Temperature from 520° C.)

Aged 0 Hr. at Quenching Temperature. Hours Aged at 20° C.	Quenched to 100° C. Aged at 20° C.			Quenched to 150° C. Aged at 20° C.			Quenched to 200° C. Aged at 20° C.			Quenched to 230° C. Aged at 20° C.		
	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness
0	41,800	27.0	20.0	43,250	23.5	23	42,950	20.5	23	41,950	23.5	24
0	41,250	22.0	21.0	43,550	23.0	23	43,600	19.5	23	42,500	26.0	24.5
½							49,300	15.5	39–40	45,500	21.5	25
½							50,450	14.0	39	44,900	26.0	25
1	45,750	21.5	25	44,500	26.0	25.5	49,750	15.0	37–39	44,100	22.5	25–28
1	45,025	22.0	24	44,050		25.0	48,550	15.0	36–37	45,000	22.0	26
1½	44,900	19.0	24									
1½	44,450	23.0	24									
2	44,550	23.0	24	43,850		24.0	50,100	16.0	37	44,850		25
2				44,600	27.0	23.5	49,000	11.5	37	43,700	23.0	22–25
3							49,100	16.5	37			
3							50,950	16.0	37–39			
19	44,700	24.5	25				48,850	16.0	37			
19	47,100	24.5	27				48,950	12.5	38			
48	46,950	25.5	26				49,250	16.0				
48	47,000	22.0	26				48,950	14.0				
96	47,000	22.0	26	51,500	20.0	31				51,600	25.0	30
96	48,250	22.0	26	52,500		30				50,400	24.0	30

at temperatures above 100° C., and that at aging temperatures above 140° C. the hardness eventually drops after reaching its maximum.

Fig. 5 shows the results of an experiment similar to that of Fig. 2. The strips were quenched from 515° C. in boiling water and aged for 20 hr. thereafter in a furnace giving a temperature gradient from one end to the other of the sample. For a time of aging of 20 hr. the hardness first increases with the temperature to a maximum at about 175° C. and then decreases. Above this temperature annealing sets in.

Effect of Temperature of Quenching Bath

Table 6 shows the effect of temperature of the quenching bath upon samples of A-1-12 quenched from 520° C. The tensile strength of the

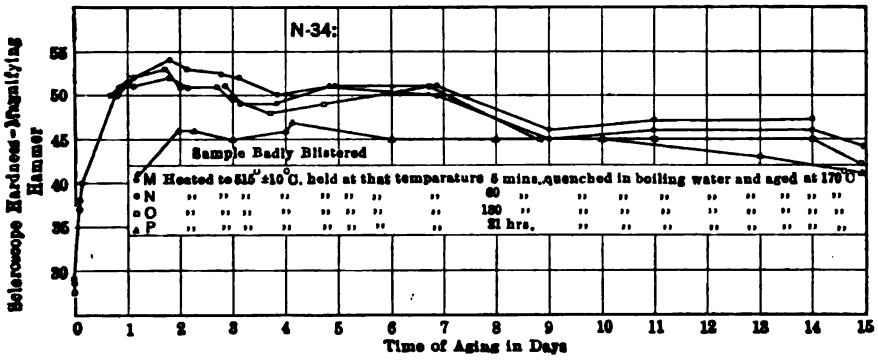

FIG. 6.—EFFECT ON SCLEROSCOPE HARDNESS OF HOLDING SPECIMENS FOR SOME TIME AT QUENCHING TEMPERATURE BEFORE QUENCHING.

alloys, as well as the elongation, increases with the time of aging. There is no marked effect of the temperature of the quenching bath indicated in these results; those samples quenched to 150° C. gave practically the same results as those quenched to 230° C., although there is a slight improvement in the tensile properties of those quenched to 150° C. over those quenched to 100° C.

In Table 7 are shown results of tests to determine the effect of aging at room temperature after aging at the temperature of the quenching bath. It will be noted that there is only a slight increase in the strength of the alloy produced by aging at 20° after aging at the temperature of the quenching bath.

Effect of Prior Heating at Quenching Temperature

Fig. 6 shows the results of hardness measurements on samples held at the quenching temperature for varying periods of time, quenched and aged at 170° C. The samples held from 5 to 180 min. at the quenching temperature give values of the hardness differing by less than the prob-

able error of measurement. The low values found on the sample held 21 hr. are due probably to the blistering which was noticed in the sample.

Effect of Preheating to 515° C. before Quenching from Lower Temperatures

In Figs. 7 and 8 are shown the results of experiments to determine whether preheating to a temperature higher than the quenching one before quenching gave a hardness different from that obtained by heating merely to the quenching temperature.

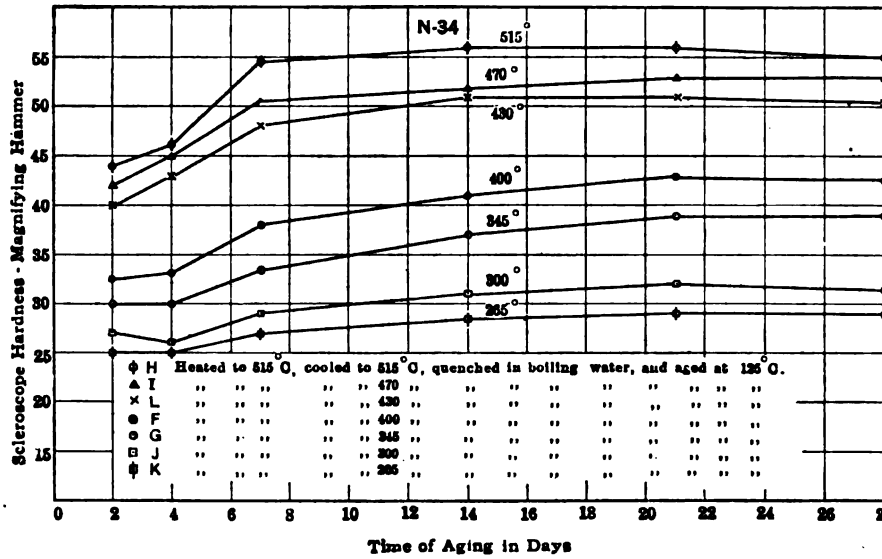

FIG. 7.—EFFECT ON SCLEROSCOPE HARDNESS OF PREHEATING SPECIMENS HIGHER THAN QUENCHING TEMPERATURE, COOLING TO LATTER, THEN QUENCHING AND AGING.

Although owing to a slight difference in the aging conditions, the comparison is not quite definite, it is obvious (1) that the hardness obtained by heating to 515° C., cooling to a temperature t (when $t<515°$ C.), and quenching, is always greater than that obtained by quenching from $t°$; and (2) that whether the specimen is preheated or not to a higher temperature before quenching from some lower temperature, the hardness obtained increases with higher quenching temperatures.

MISCELLANEOUS TESTS

In Table 8 are shown the results of a number of tests of alloy N-34, including determinations of the proportional limit of several heat-treated samples. Inasmuch as so many of the tests made during this investigation were measurements of scleroscope hardness, a comparison was made between the hardness and the tensile proportional limit of some specimens

of N-34 during aging at two temperatures. The results are shown in Fig. 9, the curves in each show quite close parallelism.

Experiments were conducted on specimens of A-1-12 to ascertain whether the hardening during aging could be hastened by vibration. The results of several such tests in which the vibration was produced by

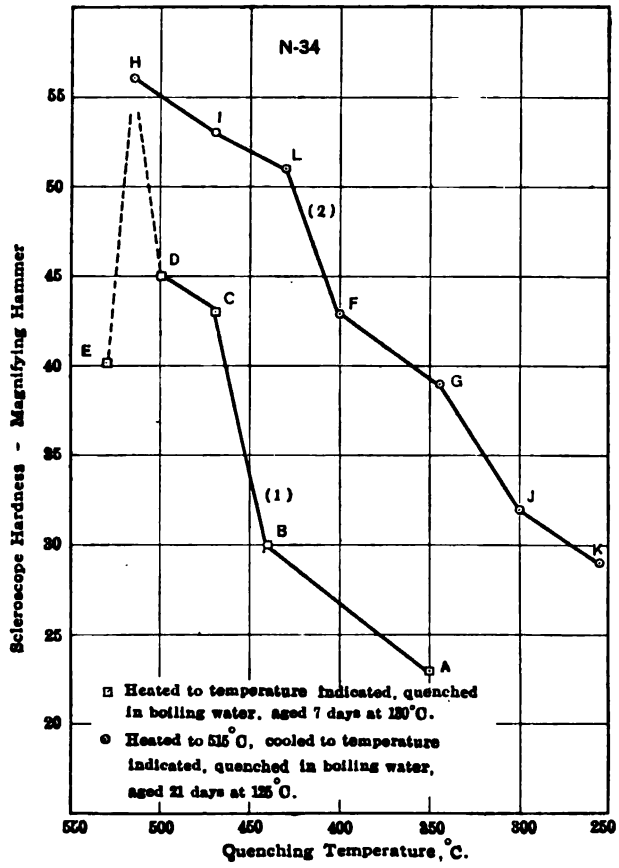

FIG. 8.—COMPARISON OF SCLEROSCOPE HARDNESS OF SPECIMENS OF ALLOY N-34. (1) HEATED TO QUENCHING TEMPERATURE, QUENCHED, AND AGED 7 DAYS AT 130° C., AND (2) HEATED TO 515° C., COOLED TO QUENCHING TEMPERATURE, QUENCHED, AND AGED 21 DAYS AT 125° C.

a bell clapper indicated that there was no difference in the rate of hardening between vibrated and quiet specimens.

Density and Dilation

The density was determined of samples of N-34 in different conditions; Table 9 gives the results of these tests. In some cases one dimension of the specimen was determined also, and its changes recorded in the

TABLE 7.—*Effect of Aging at Room Temperature (20° C.) after Aging at Temperature of Bath*
(Specimen of Alloy A-1-12 Quenched from 520° C.)

Hours Aged at 20° C.	Quenched to 100° C. Aged at 20° C.			Quenched to 150° C. Aged at 20° C.			Quenched to 200° C. Aged at 20° C.			Quenched to 230° C. Aged at 20° C.		
	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Scleroscope Hardness
Aged ½ Hr. at Quenching Temperature.												
¼										45,150	10.0	35
½										46,250	10.0	37
½				49,100	26.0	31				42,850	12.0	32
1				50,500	23.0	31				42,600	10.5	35
2				49,500	25.5	28				45,750	9.0	36
2				49,600	26.0	28–30				46,100	10.5	36
3												
3												
96				*50,800		31	53,200	10.0	40	48,500	10.0	34
96				*52,000	25.5	31	51,700	12.0	41	46,450	8.5	34
Aged 1 hr. at quenching temperature.												
										(Aged ½ hr. at 20° C.)		
2				49,250	25.5	31				(47,050	9.5	38–41)
2				50,000	25.0	31				(47,300	9.5	36–39)
96				*52,500		31	50,600	9.0	43	48,600		37
96				*52,500		31	49,400	7.0	41	48,550		39
Aged 2 hr. at quenching temperature.												
										(Aged ½ hr. at 20° C.)		
2				51,450	24.5	33				(47,600	9.0	37)
2				48,500	23.0	33				(47,100	9.0	37)
96	48,900	24.5	28.0	*54,600	24.0	32	52,150		44	50,400	8.5	38
96	47,450		27	*53,850	22.5	32	53,550	11.0	42	50,750		41
Aged 3 hr. at quenching temperature.												
2				52,450	22.0	34						
2				49,900	23.0	34						
96							54,950		43			
96				*56,250	19.5	32.5	54,550	10.0	44			
Aged 19 hr. at quenching temperature.												
96	51,000	24.5										
96	51,550											
Aged 48 hr. at quenching temperature.												
96	52,000	20.5										
96	51,600	23.5										

* These specimens were aged at 20° C. for 120 hr.

TABLE 8.—*Effect of Varying Aging Temperature and Time of Aging on Tensile Properties of Aluminum Alloy Sheet.*[1] *Alloy N-34.*

No.	Thickness of Sheet, Inch	Heat Treatment			Scleroscope Hardness Magnifying Hammer	Ultimate Strength, Lb. per Sq. In.	Proportional Limit, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Remarks
		Quenched from C°	Aged						
			at ° C.	Days					
14	0.034	515		0	26		17,000	5	Broke at extensometer contact.
15	0.034	515		0	26	38,200	17,000	6	Broke at extensometer contact.
24	0.034	515	105	2	39	52,900	27,000	7	Broke at extensometer contact.
25	0.034	515	105	2	39	54,900	29,000	7	Broke at extensometer contact.
26	0.034	515	105	4	39	55,500	27,000	9	Broke at extensometer contact.
27	0.034	515	105	4	39	55,200	26,000	8.5	Broke at extensometer contact.
28	0.034	515	105	7	38	63,200		23	No extension measurements.
29	0.034	515	105	7	38	56,200	29,000	9	Broke at extensometer contact.
30	0.034	515	105	9	42	61,200	30,000	16	Extensometer attached to flat surfaces. Broke at gage point.
31	0.034	515	105	9	41	60,600	29,000	14.5	Extensometer attached to flat surfaces. Broke at gage point.
32	0.034	515	105	14	40	62,200	31,000	21	Extensometer attached to flat surfaces.
33	0.034	515	105	14	41	61,600	33,000	23	Extensometer attached to flat surfaces.
16	0.034	515	125	2	41–46	49,500	27,000	2.5	Broke at extensometer contact.
17	0.034	515	125	2	42–50	54,500	32,000	3	Broke at extensometer contact.
18	0.034	515	125	4	45–50	58,200	30,000	3	Broke at extensometer contact.
19	0.034	515	125	4	45–50	58,500	33,000	4	Broke at extensometer contact.
20	0.034	515	125	7	44–47	60,000	39,000	4.5	Broke at extensometer contact.
21	0.034	515	125	7	42–48	58,000	37,000	4	Broke at extensometer contact.
34	0.087	515	125	7	46–50	61,200	32,000	18	Extensomotor attached to flat surface.
35	0.087	515	125	7	47–52	62,000	31,000	18	Extensometer attached to flat surface.
22	0.034	515	125	14	47–52	64,900	37,000	11	Extensometer attached to flat surface.
23	0.034	515	125	14	47–54	61,500	35,000	3	Extensometer attached to flat surface. Fractured at blister.
2	0.034	515	150	2	50	51,110		16	No extension measurements.
3	0.034	515	150	2	49	50,940		16.5	No extension measurements.
4	0.034	515	150	4	50	59,800		11.5	No extension measurements.
5	0.034	515	150	4	50	61,500	41,000	6	Broke at extensometer contact.
6	0.034	515	150	6	50	63,800		6	No extensometer measurements.
7	0.034	515	150	6	50	62,200	43,000	6.5	Broke at extensometer contact.
1	0.087	515	170	2	50	63,900		10	No extension measurements.
8	0.034	515	170	2	51.5	51,420		10.5	No extension measurements.
9	0.034	515	170	2	51.5	51,850		10	No extension measurements.
10	0.034	515	170	2	51.5	50,760		9.5	No extension measurements.
11	0.034	515	170	4	44	58,200		9.5	No extension measurements.
12	0.034	515	170	4	44	55,500		5	No extension measurements.
13	0.034	515	170	4		57,300	34,000	6	Broke at extensomoter contact.

[1] Where two values of hardness are given, the lower one shows the hardness of the end near the door of the furnace in which the sample was heated for quenching and the other value is the hardness of the opposite end, the difference in hardness being the result of a temperature gradient in the furnace. All specimens in this condition broke at the soft end and hence their tensile properties are hardly as high as can be expected of the material.

TABLE 9.—*Density and Dilatation of Duralumin*

Sample	Treatment	Density	Length, Inches
N34 D-1	Quenched; not aged	2.762	
N34 D-1	Same as above, after aging at 150° C.	2.762	
N34 D-2	Annealed, after rolling, at 515° C.	2.759	
N34 D3	As rolled, 0.033 in. thick	2.754	12.014
N34 D3-a	Same after annealing at 500°	2.742	12.024
N34 D3-a	Annealed at 530° C.	.....	12.0477
N34 D4	As rolled, 0.088 in. thick	2.750	11.982
N34 D4-a	Same after annealing at 500°	2.747	11.982
N34 D4-a	Annealed at 530° C.	.....	11.9973
N34 D5	As rolled, 0.25 in. thick	2.764	11.9954
N34 D5-a	Same after annealing at 500°	2.762	11.9963
N34 D5-a	Annealed at 530° C.	.....	12.0019

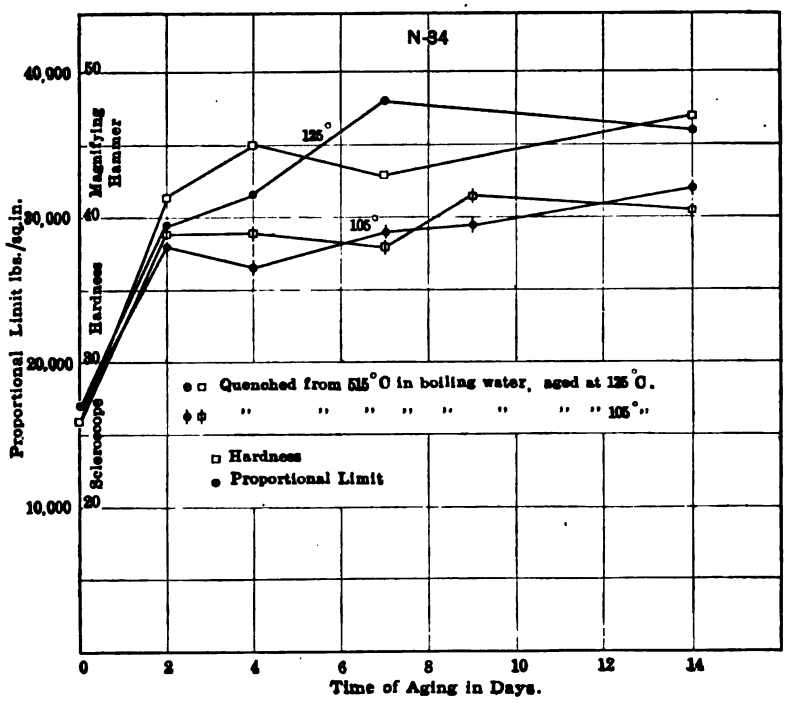

FIG. 9.—COMPARISON DURING AGING OF SCLEROSCOPE HARDNESS AND TENSILE PROPORTIONAL LIMIT. (ALLOY N-34.)

fourth column of the table. The changes in density are quite small as the material undergoes heat treatment or annealing, except when the temperature exceeds from 520 to 530° C., the temperature of eutectic melting, when a marked increase in length is noted.

The linear expansion, up to 520° C., was determined on two bars of N-34, one as rolled, the other after heat treatment consisting of quenching from 520° C. and aging two days at 120° C. The expansion curves are given in Fig. 10, and show irregularities in the neighborhood of 300°.

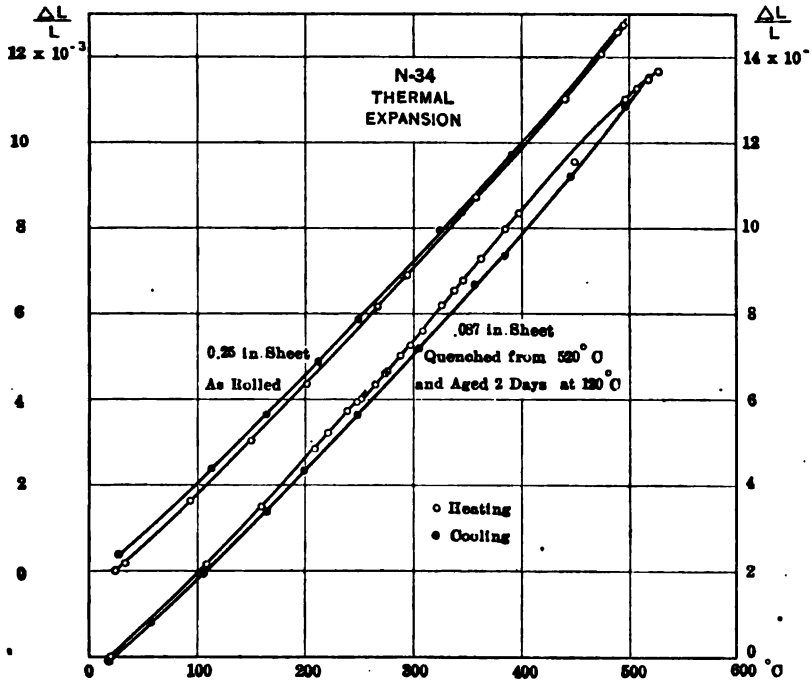

FIG. 10.—LINEAR EXPANSION OF N-34, 0 TO 500° C.

Electrical Resistivity

Electrical resistivity measurements were made in vacuo by the method described by Burgess and Kellberg[8] on 0.25-mm. wire drawn from a cylinder cut out from ¼-in. (6.35-mm.) sheet of C-11 over the temperature range 0 to 530° C. It was necessary, however, to bring both of the aluminum-alloy leads out of the thermometer as it was impossible to weld them to platinum. The data obtained from the first run is plotted as resistance of aluminum alloy against temperature in Fig. 11.

[8] *Sci. Paper* No. 236, U. S. Bureau of Standards (1914).

The change in direction of the resistivity curve at about 300° is quite evident and indicates a change in the constitution of the alloy. It is evident both on heating and cooling, although a change in resistivity at room temperature has taken place resulting from the annealing produced during the series of measurements.

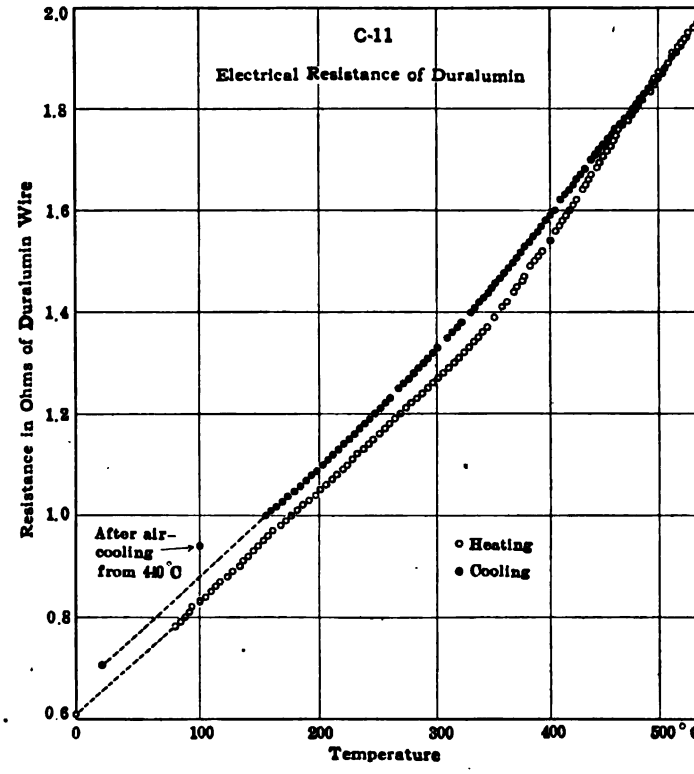

FIG. 11.—ELECTRICAL RESISTIVITY OF C-11, 0 TO 530° C.

Following this run the material was heated to 440° C. in its tube and cooled in air. The cooling was fairly rapid as the outside diameter of the quartz tube was only 8 mm. The tube was then put in a steam bath and resistance measurements taken as follows:

Time in Steam Bath, Hours	Pt Resistance	Al Resistance	Time in Steam Bath, Hours	Pt Resistance	Al Resistance
0	1.7302	0.9035	4½	1.7300	0.9063
½	1.7302	0.9047	6	1.7301	0.9069
1	1.7302	0.9051	7	1.7301	0.9068
2	1.7297	0.9054	11	1.7298	0.9069
3	1.7301	0.9060			

The specific resistance of this alloy was determined on a wire drawn to 0.254 mm. diameter and annealed at 400° C. It was found to be 3.35 microhm-cm.

Mechanism of Hardening During Aging after Rapid Cooling

Apparently no attempt has been made to develop an explanation for the changes in the physical, particularly mechanical, properties of this alloy during aging after rapid cooling. The changes that take place are quite marked and definite and must correspond to some quite as definite changes in the structure and constitution of the alloy, or at least to profound molecular changes. If we are not able to show that actual phase changes take place during aging, we must ascribe these changes in physical properties to alterations in the atomic or molecular structure. All evidence the authors have been able to find or to accumulate seems to indicate that the hardening during aging is actually accompanied by a phase change within the alloy. In so far as it can be said then that this phase change causes the hardening, for the reason that it accompanies it, this phase change may be regarded as its active cause.

Elsewhere,[9] the authors have determined the solubility at different temperatures in aluminum of $CuAl_2$ and of Mg_4Al_3, the aluminum-rich compounds of the copper-aluminum and magnesium-aluminum binary alloy series respectively. The solubility-temperature curves of these compounds are reproduced in Figs. 12 and 13; the solubility of both compounds diminishes rapidly with lowered temperature.

Upon slowly cooling an alloy containing 3 per cent. of copper from 500° C., the $CuAl_2$ precipitates from solid solution to maintain equilibrium along the line *be*. The alloy so obtained is soft and does not harden upon aging. Rapid cooling of the same alloy from 500° C. by quenching, partly or wholly suppresses this precipitation of $CuAl_2$. If the alloy is held at a low temperature, such as at that of liquid air (−180° C.), no further hardening takes place upon aging. The alloy is not in equilibrium but the rate of nuclear formation of $CuAl_2$ is so small that no $CuAl_2$ precipitates to bring about equilibrium. If, however, the temperature of the alloy is raised to 100° C. or even to ordinary room temperature, according to the theory which the authors propose, the mobility of the molecules becomes sufficiently great that precipitation of the $CuAl_2$ takes place in the form of very fine particles of colloidal dispersion. To this precipitation is due the hardening during aging of duralumin. The evidence

[9] P. D. Merica, R. G. Waltenberg, and J. R. Freeman, Jr.: Constitution and Metallography of Aluminum and its Light Alloys with Copper and with Magnesium, *Sci. Paper* No. 337, U. S. Bureau of Standards (1919). Also this volume, p. 3.

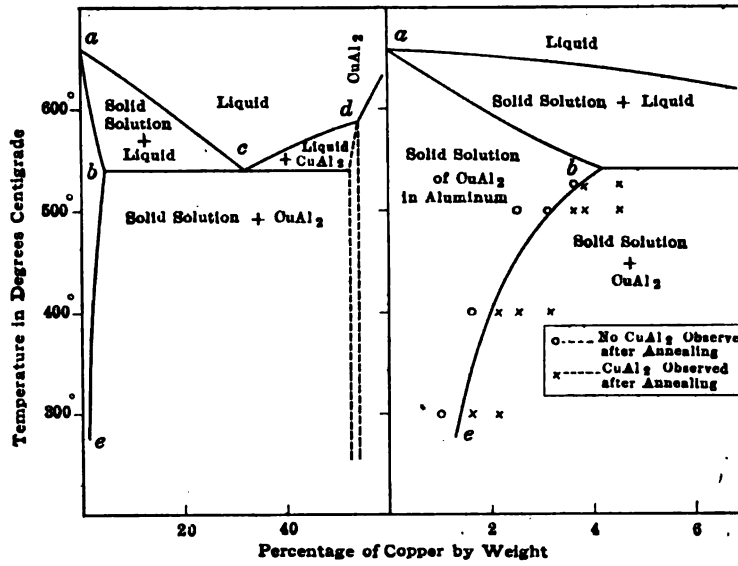

FIG. 12.—PORTION OF EQUILIBRIUM DIAGRAM OF COPPER-ALUMINUM ALLOY SERIES SHOWING SOLUBILITY CURVE *be* OF $CuAl_2$ IN ALUMINUM.

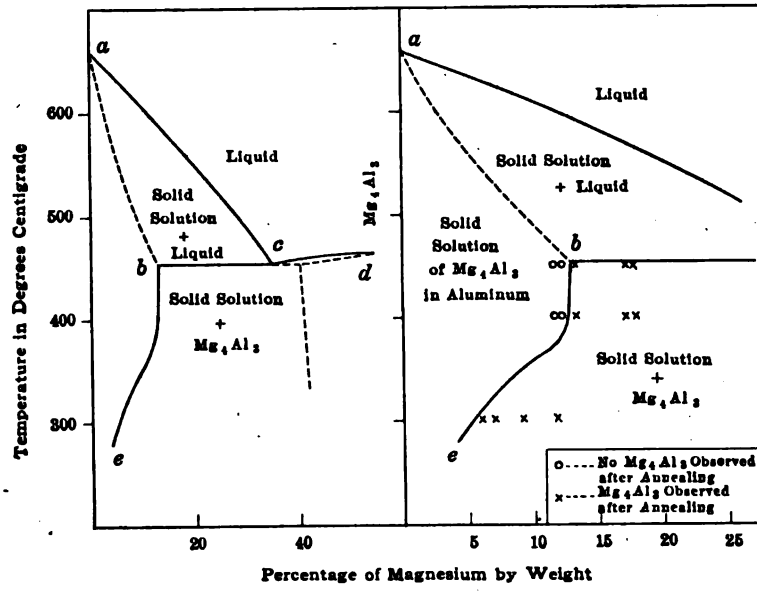

FIG. 13.—PORTION OF EQUILIBRIUM DIAGRAM OF MAGNESIUM-ALUMINUM ALLOY SERIES SHOWING SOLUBILITY CURVE *be* OF Mg_4Al_3 IN ALUMINUM.

in favor of this theory is largely of an indirect nature; the only direct confirmation of its truth is furnished by the results of thermal analysis.

Upon heating a specimen of duralumin that has been quenched from 500° C., but not aged, an evolution of heat occurs at from 250 to 275° C. This is shown in inverse-rate heating curves of three compositions,

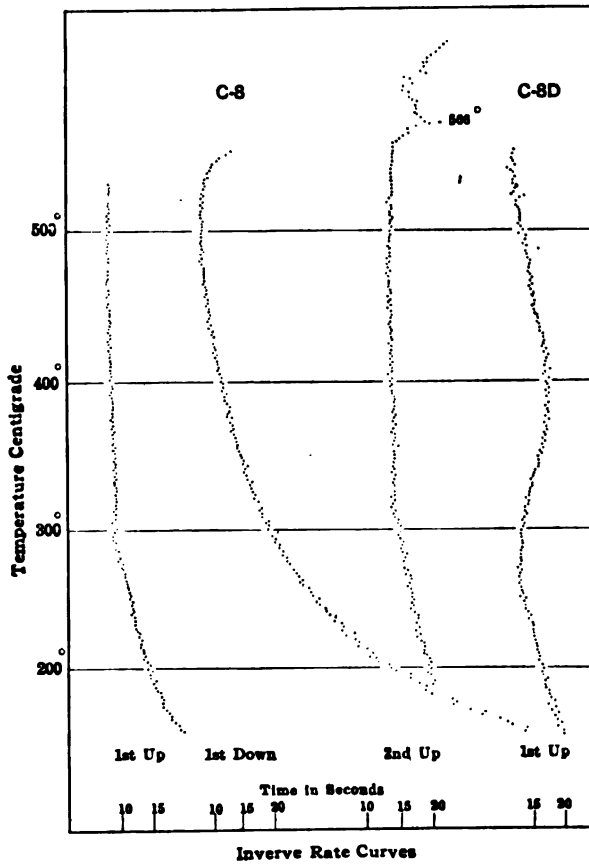

FIG. 14.—HEATING AND COOLING CURVES OF C-8. FIRST RUN UP SHOWING ARREST AT 300° C. WAS TAKEN 3 HR. AFTER QUENCHING. C-8-D IS A CURVE OBTAINED ON A QUENCHED SAMPLE AFTER AGING 18 MO. AT 20° C.

C-8, C-11, and N-34 in Figs. 14, 15, and 16. No thermal change takes place upon cooling the same specimen, provided it has not been heated beyond 520° C. Upon reheating the same slowly cooled specimen, no evolution of heat is found corresponding to that upon the first heating. Without doubt, therefore, a chemical reaction takes place at 250 to 275° C. upon heating the quenched sample with evolution of heat; *i.e.*, indicating

the formation of stable from unstable phases, not a transformation of stable to other stable phases, the two systems being in equilibrium during the transformation. Such a transformation must take place with heat absorption upon raising the temperature.

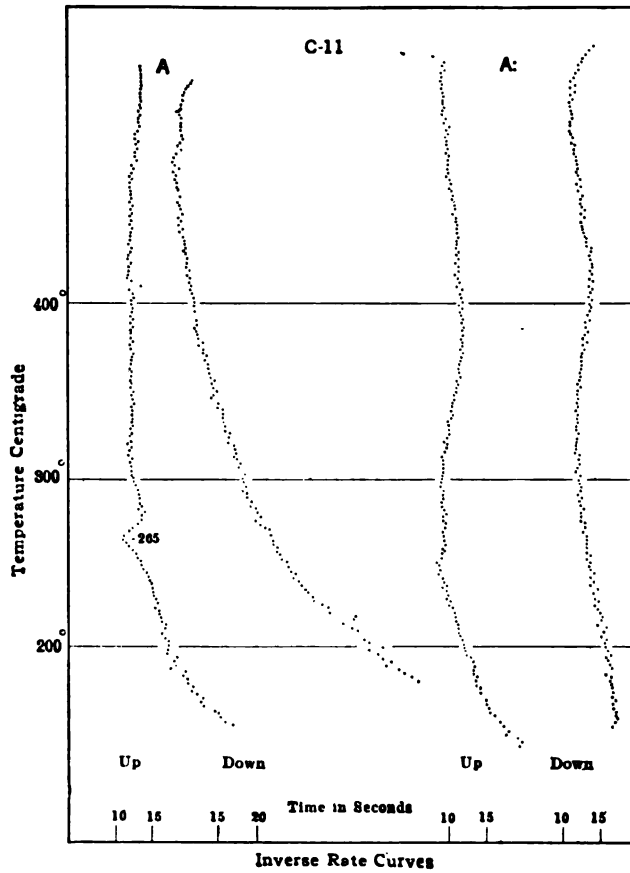

FIG. 15.—HEATING AND COOLING CURVES OF C-11. FIRST RUN UP ON C-11-A SHOWS AN ARREST AT 265° C. IN A SAMPLE THAT HAD BEEN QUENCHED AND THEN AGED 12 DAYS AT 20° C. SECOND RUN UP, MARKED C-11-A, SHOWS PRACTICALLY NO ARREST IN A SAMPLE THAT HAD BEEN QUENCHED IN BOILING WATER AND AGED 10 DAYS AT 120° C.

A specimen that has been quenched and aged at from 100° to 150° C. to secure maximum hardness shows little or no evolution of heat upon heating, see curves in Figs. 14, 15, and 16. Whatever may be the chemical reaction that is indicated on the first heating curve of a quenched specimen, it has taken place during the aging of the specimen, during which the hardening also occurs; stable phases have formed and the subsequent

heating curve shows no arrest corresponding to that of the quenched specimen.

This chemical reaction can hardly be other than the precipitation of $CuAl_2$ from its super-saturated solution in aluminum, although direct visual evidence bearing on this question is also lacking. In describing the attempt made to recognize microscopically the phase change during

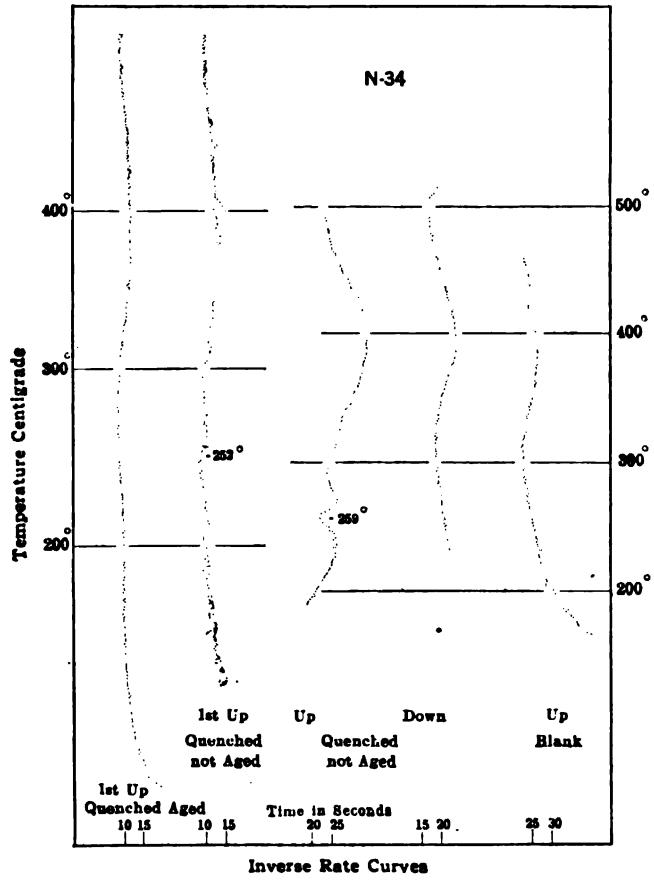

FIG. 16.—HEATING AND COOLING CURVES OF N-34 SHOWING INVERSE ARREST IN QUENCHED SAMPLES THAT HAD NOT BEEN AGED BUT NO ARREST IN SAMPLES THAT HAD BEEN AGED AFTER QUENCHING.

aging just predicated, a digression must be made in order to discuss the general features of the microstructure of duralumin, which has apparently never been done before.

Structure of Duralumin

The microstructure of duralumin may be developed either by etching in a relatively concentrated solution of sodium hydroxide, NaOH, a

dilute solution of hydrofluoric acid, HF, or in a dilute solution of NaOH. The grain structure of the alloy is best developed by the two former solutions; 10 per cent. NaOH and 5 per cent. HF are generally used for this purpose. For the identification and study of the different microscopic constituents of the alloy, a 0.1 per cent. solution of NaOH has,

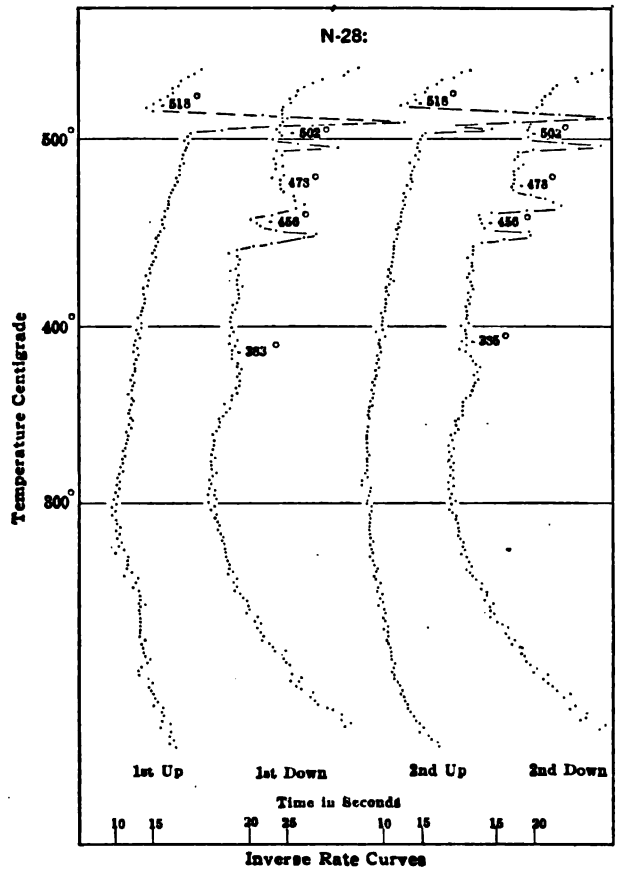

FIG. 17.—HEATING AND COOLING CURVE OF N-28. (Cu 4.98 PER CENT., Mg 2.41 PER CENT.)

however, shown itself much superior to the former ones, and this solution has been used in most of the authors' investigations.

Duralumin after rolling shows a structure similar to that in Fig. 18, which is quite typical. Fig. 19 shows the same alloy at a higher magnification. Grains of aluminum (in which are dissolved Si, $CuAl_2$, and Mg_4Al_3) are surrounded by strings of islands of eutectic ($CuAl_2$-aluminum, $FeAl_3$-aluminum and possibly others), which are white in Fig. 18. Upon examination under a higher power, the eutectic is seen to consist of

two constituents; one a brownish color, the other white. These two constituents are evident in Fig. 19. In another article by the authors,[10] these two constituents have been identified as $FeAl_3$ (brown) and $CuAl_2$ (white), respectively. Quite often, but not always, the $FeAl_3$ surrounds the $CuAl_2$, as is shown in the figure.

FIG. 18.

FIG. 19.

FIG. 18.—ROLLED DURALUMIN N-34. ETCHED WITH 0.1 PER CENT. NaOH. × 65.
FIG. 19.—ROLLED DURALUMIN, N-34(E4). ETCHED WITH 0.1 PER CENT. NaOH. × 650.

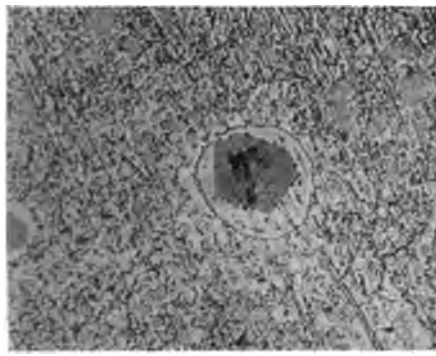

FIG. 20.

FIG. 21.

FIG. 20.—SPECIMEN OF N-28 CONTAINING Cu AND Mg; SHOWING ISLAND OF Mg_2Si (DARK) WITHIN ONE OF $CuAl_2$ (WHITE). × 650.
FIG. 21.—SAMPLE OF DURALUMIN, E3; SHOWING $FeAl_3$ AND $CuAl_2$ EUTECTIC, AND FINE PARTICLES THROUGHOUT GROUNDMASS. × 650.

Besides these two constituents, a third, of pronounced bluish color, is visible. This is readily distinguished under the microscope, not always so readily in a photograph; it is seen within an island of $CuAl_2$ in Fig.

[10] Reference 9.

20. In the same article, the authors have expressed the opinion that this is Mg_2Si; it occurs only in alloys containing magnesium.

Upon still closer observation, the grains of aluminum solid solution are seen to contain minute particles of a constituent, shown in Figs. 21

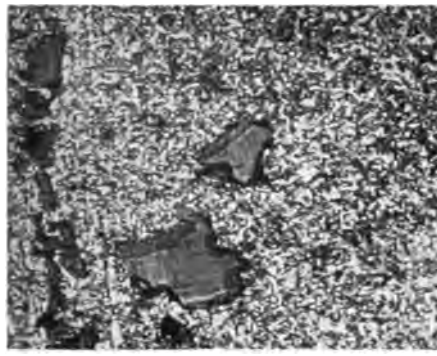

FIG. 22.

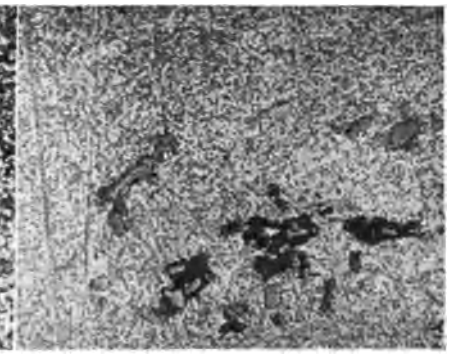

FIG. 23.

FIG. 22.—SAMPLE OF E3, SAME AS FIG. 21. × 1285.
FIG. 23.—SAMPLE OF DURALUMIN E3-F, AFTER ANNEALING 20 HR. AT 500° C., QUENCHING AND AGING AT ROOM TEMPERATURE. × 650.

FIG. 24.

FIG. 25.

FIG. 24.—SAME MATERIAL AS IN FIG. 23. × 650.
FIG. 25.—SAMPLE OF DURALUMIN, E4-F, AFTER ANNEALING 20 HR. AT 500° C., QUENCHING AND AGING AT ROOM TEMPERATURE. × 650.

to 25, which are so small that it is impossible to identify them with certainty. Inasmuch as they occur also in aluminum itself, they must consist, in part at least, of the compound *X* (of iron, silicon, and probably also, aluminum,[11]) and possibly $FeAl_3$; probably $CuAl_2$ is also present

[11] Reference 9.

in this form. All of this generation of particles have undoubtedly separated during cooling from a solid solution in aluminum at higher temperatures.

The visible structure of duralumin changes but slightly on heat treatment. Rolled duralumin consists of elongated grains. Upon heating such material to 500° C., recrystallization of the aluminum (solid solution) grains first occurs, and the fine grains so formed increase in size. This growth is naturally interrupted by quenching. Immediately after quenching, therefore, the grains may be either larger or smaller than the original ones, depending on the period of heating at 500° C. and the rate of heating to that temperature. During subsequent aging, the grains do not change in size. Heating to 500° C. also results in the solution of some or all of the $CuAl_2$ eutectic grains seen in the rolled material, to correspond to equilibrium. The $FeAl_3$ does not dissolve.

If there occurs during the aging of duralumin after quenching a gradual precipitation of $CuAl_2$ particles to correspond to its diminished solubility at the lower temperatures, one would expect to be able to observe some difference between the microstructure of the quenched unaged specimen and that of the quenched one after thorough aging. The particles of $CuAl_2$ may quite well be too small to be resolvable microscopically, but the presence of a large number of such colloidal particles might be expected to accelerate the etching of the specimen; at least troostite etches much more readily than martensite or sorbite, and it is considered quite generally to consist of a colloidal solution of Fe_3C in alpha iron. Samples of N-34, some of which had been heated at 500° C. quenched in water and immediately etched, and some of which had been subsequently aged at 130° C. after identical treatment to develop maximum hardness, were carefully compared in their appearance after etching in the same solution (0.1 per cent. NaOH) and for the same periods of time. No difference was observed in the structure nor in the general shades of the etched surfaces of these two groups of specimens. The authors have to date, therefore, no direct structural evidence of the precipitation of $CuAl_2$ during aging of duralumin.

A difference in the rate of etching of quenched unaged, and of quenched and aged may quite possibly be obscured by the presence of other constituents in fine dispersion, present in both cases. It was noted above that there are always present a number of fine particles of the *X* constituents. A structural study of duralumin made with pure aluminum, free from iron and silicon, might yield more positive results.

It is interesting to note that although the velocity of nuclear formation of $CuAl_2$ at temperatures from 20° to 400° C. seems to be quite normal, judging by thermal analysis, the velocity of crystallization or of coalescence of the nuclei is evidently quite remarkably small. Thus it was

found[12] that there was no visible precipitation of $CuAl_2$ in an alloy containing 3 per cent. of copper upon annealing at 300° C. for 20 hr., after obtaining all of the $CuAl_2$ in solution by annealing at 500° C. Only by very slow cooling from 500° to 20° C. could a visible precipitate of $CuAl_2$ be produced. Slow velocities of crystallization seem to be characteristic both of $CuAl_2$ and of aluminum.

Although it cannot be directly proved that the thermal arrest at about 250° C. noticed upon heating a quenched unaged specimen of duralumin is due to the precipitation of $CuAl_2$, no evidence directly contradicts this assumption, which is in entire accord with our knowledge of the equilibrium within the alloy, and this arrest cannot be assigned to any other phase change.

It has been shown by many previous investigations, and confirmed by the authors, that aluminum undergoes no transformation in the solid state between ordinary temperatures and its melting point. No other phase changes could occur in the main mass of duralumin, the grains of solid solution, therefore, except those of solution or precipitation of $FeAl_3$, of the *X* compound, of $CuAl_2$, of Mg_4Al_3, or of Mg_2Si within the grains. Aluminum, which contains the same amounts of $FeAl_3$ and of the *X* compound as does duralumin, is not altered by heat treatment as is duralumin, nor does it show a reverse heat effect upon heating as does the latter. This heat effect must, therefore, be due to the precipitation of $CuAl_2$, Mg_4Al_3, or Mg_2Si. But the alloys containing only magnesium, in amounts up to 3 per cent., also do not harden upon aging. There remains only the precipitation of $CuAl_2$ with which to explain this heat effect.

The theory outlined above of the mechanism of the hardening of duralumin during aging most readily explains the interesting fact discovered by Mr. Blough, and confirmed by the authors, that the amount of hardening during aging increases as the temperature of quenching increases. At higher quenching temperatures, more and more $CuAl_2$ is dissolved in solid solution. After quenching the $CuAl_2$ is in excess of its solubility; the higher the quenching temperature the greater is the excess, and this is precipitated during aging. The hardening is in proportion to the amount of the highly dispersed $CuAl_2$ formed.

If this theory is accepted for the moment, it is interesting to consider the effect of degree of dispersion upon hardness in the case of a solid solution, in this case of $CuAl_2$ in aluminum. Duralumin immediately after quenching is generally softer than it is in the annealed condition. Thus alloy C-11, in the form of sheet, gave the following values of hardness:

	Annealed at 300°	Quenched, but not Aged	Quenched and Aged 8 Days
Scleroscope hardness, magnifying hammer.....	17	16	35

[12] Reference 9.

This is probably due to the fact that a specimen, as ordinarily cooled after annealing, still contains some dissolved $CuAl_2$ in excess of its solubility; the material hardens slightly during cooling. Specimens cooled extremely slowly give a scleroscope hardness of from 7 to 10, much lower than that of the quenched, unaged ones.

Upon aging a quenched specimen at 200° C., for example, the hardness first increases to a maximum and afterward decreases. During that aging there has been first a formation of fine nuclei of $CuAl_2$ followed by coalescence of these particles into ones of larger size. There is, therefore, a certain average size of particle of $CuAl_2$, for which the hardness of the material is a maximum; atomic dispersion of the solute, $CuAl_2$, is not the dispersion that produces the maximum hardness, but some intermediate one between it and that at which the particles become visible by ordinary means.

It is interesting to observe that the properties of other light alloys of aluminum are influenced by heat treatment and aging. Thus Rosenhain and Archbutt[13] have found that the tensile strength of sand-cast aluminum-zinc alloys increases upon aging. In another article[14] by two of the authors, it has been shown that whereas alloys of aluminum-magnesium, aluminum-manganese, aluminum-manganese-magnesium, and aluminum-nickel do not harden upon quenching and aging; those of aluminum-magnesium-nickel do. The solubility of zinc in aluminum decreases from 40 per cent. at the eutectic temperature to about 25 per cent. at 256° C. and is probably much less at still lower temperatures. As in the case of the copper-aluminum alloys, decreasing solubility at lower temperatures of the constituent, $CuAl_2$ or zinc, is accompanied by the possibility of hardening by quenching and aging.

Inasmuch as the aluminum-nickel-magnesium alloys also harden by aging, we may expect an appreciable solubility of $NiAl_3$ in solid aluminum at higher temperatures. The solubility of $MnAl_3$ is undoubtedly quite low.

Analogy Between Hardening of Duralumin and That of Steel

The hardening of duralumin upon the basis of this hypothesis presents an interesting analogy with that of steel. The hardening of steel is due to the partial or entire suppression of the eutectoid transformation; most recent thought regards it as due more directly to the suppression of the cementite precipitation (as pearlite), the transformation of γ and α iron having taken place at least in part. The partial suppression there-

[13] Report to the Alloys Research Committee, *Proc.* Inst. Mech. Eng. (1912) 319.
[14] P. D. Merica, A. G. Waltenberg and A. N. Finn: *Op. cit.*

fore of the precipitation of a compound from a solid solution is common both to rapidly cooled steel and to duralumin.

A sample of steel that has been hardened but not tempered shows an evolution of heat upon heating[15] through its tempering range exactly as does duralumin. This is due to the precipitation of Fe_3C in finely divided form in the case of steel exactly as it seems to be due to that of $CuAl_2$ in duralumin.

During the tempering or aging of steel at from 100° to 300° C., the hardness usually decreases immediately; *i.e.*, the maximum hardness of steel is obtained by quenching alone whereas that of duralumin is produced by tempering after aging. In the case of some high-carbon steels (from 0.9 to 1.7 per cent. C), however, the hardness increases during tempering after quenching exactly as in the case of duralumin.[16] The maximum hardness in hardened steel increases with the carbon content, as it does in duralumin with the copper content. It has been found that tool steel containing tungsten undergoes an increase of hardness during tempering at from 400° to 650° C. after quenching from 1350° C.[17]

Eutectic Structure and Influence of Magnesium

There is one fact that is not readily explained by the authors' hypothesis. Although alloys containing only magnesium and no copper do not harden and alloys containing only copper with no magnesium do harden, those containing both copper and magnesium undergo a much greater hardening than do those with copper alone. Magnesium, therefore, exerts no effect by itself in this direction and is not essential to the hardening power, but it materially increases the effect of the copper. The hypothesis developed above does not indicate any reason for this effect.

The authors are of the opinion that the influence of the magnesium is of a secondary nature. Thus, it seems probable that some magnesium unites with the silicon present to form Mg_2Si, the blue constituent always found in alloys containing magnesium. The removal of the silicon in this manner may be the direct cause of the resultant increase of hardening effect. This would agree with the observed fact that with the usual silicon content, 0.5 per cent. magnesium is enough fully to develop the partly latent hardening power of the copper-aluminum alloys; the addition of more magnesium produces a somewhat harder alloy in all

[15] H. Scott: Effect of Rate of Temperature Change on Transformations in Alloy Steel, *Sci. Paper* No. 335, U. S. Bureau of Standards (1919); also *Trans.* (1920) **62**, 699.

[16] E. Maurer: Härten und Anlassen von Eisen und Stahl, *Metallurgie* (1909) **6**, 33.

[17] Edwards and Kikkawa: *Jnl.* Iron and Steel Inst. (1915) **92**, 6.

conditions but does not materially increase the hardening effect. This is shown by the following comparison:

Alloy	Copper	Magnesium	Tensile Strength Annealed, Pounds per Sq. In.	Tensile Strength Hardened, Pounds per Sq. In.	Increase in Tensile Strength upon Hardening, Per Cent.
C-11	2.6	1.3	35,000	56,000	60
C-12	3.2	0.5	23,000	49,000	110

Consideration of the test results of Table 2 shows that magnesium hardens the aluminum matrix considerably even in the annealed condition. It is probable that the alteration of this matrix affects markedly the dispersion of the precipitation of $CuAl_2$ during aging and, consequently, the mechanical properties obtained.

There is another feature of the structure of duralumin that is of great importance and in which may be found some part of the explanation for the effect of magnesium. This is the manner in which the $FeAl_3$ and the $CuAl_2$ eutectics crystallize. There are several possible binary eutectics in duralumin, namely the following:

Eutectic	Eutectic Temperature, Degrees Centigrade
$FeAl_3$ + aluminum solid solution	640–650
Si (cryst) + aluminum solid solution	570–580
X compound + aluminum solid solution	610
$CuAl_2$ + aluminum solid solution	520–540
Mg_4Al_3	450
Mg_2Si	440

The amounts, by volume, of the eutectics with $FeAl_3$ and with $CuAl_2$ in ordinary duralumin are fairly large and about equal, that with Mg_2Si somewhat less, that with *X* and with Mg_4Al_3, usually, almost nil. The approximate temperatures of eutectic solidification are given above; they represent in all cases the temperatures observed in the presence of both the $FeAl_3$ and the *X* eutectic. The presence of $CuAl_2$ or Mg_2Si lowers the eutectic temperatures of the other binary eutectics. Thus in the presence of Mg_2Si, the eutectic temperature of $CuAl_2$-aluminum is reduced from 540 to 520–530° C., and this is always obtained as a thermal arrest in heating or cooling duralumin.

The order of solidification of these binary eutectics in aluminum-rich alloys is a matter of the greatest importance. Fig. 26 shows the probable form of the equilibrium at the aluminum end of the ternary system, Al-Cu-Fe. An alloy containing about 0.5 per cent. Fe and 3 per cent. Cu (*g* in the figure) would follow the line *gf-fc* upon solidification. A solid solution of aluminum with $CuAl_2$ ($FeAl_3$ is almost insoluble in aluminum) first crystallizes and the composition of the liquid changes along the curve

gf with lowering of temperature. At *f*, and along *fc*, the binary eutectic $FeAl_3$-aluminum solid solution crystallizes. The liquid remaining at *f* is contained in the interstices between the solid grains of aluminum solid solution, and the $FeAl_3$ crystallizes upon these grains at the boundary between solid and liquid. At *c*, the binary eutectic $CuAl_2$-aluminum solid solution also crystallizes with the remainder of the first eutectic. The resultant structure is shown in Figs. 19, 20, 21, 22, 23, and 24. The $FeAl_3$ often entirely surrounds and isolates the $CuAl_2$ crystals.

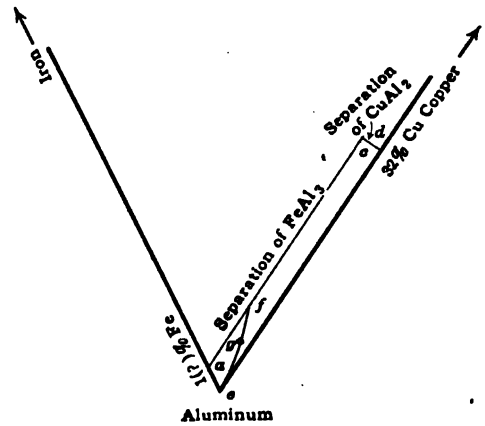

FIG. 26.—SUGGESTED FORM OF LIQUIDUS SURFACES OF TERNARY SYSTEM ALUMINUM-IRON-COPPER NEAR ALUMINUM END.

When a specimen having such a structure is heated to 500° for quenching, much of the $CuAl_2$ may be separated from the aluminum by this layer of insoluble $FeAl_3$ and is effectually prevented from dissolving. Thus E3-F, containing only 1.56 per cent. Cu, heated 20 hr. at 500° C. and quenched still contains free $CuAl_2$, although its solubility at that temperature was about 3 per cent. Its structure is shown in Fig. 23. The undissolved $CuAl_2$ (light) is surrounded by $FeAl_3$ (dark). (The other light islands are Mg_2Si, which are distinguishable under the microscope as of bluish color, but photograph light). This enclosure of the compound of one binary eutectic by that of another seems to be characteristic of light aluminum alloys.

Fig. 20 shows an island of $CuAl_2$ enclosing one of Mg_2Si. Such a structure explains probably the confusing heating and cooling thermal curves often obtained with copper-aluminum-magnesium alloys. In Fig. 16 were shown several normal heating and cooling curves for N-34 containing both copper and magnesium. The inverse heat effect in the quenched alloy at about 360° C. and the eutectic arrest at 510° C. are both visible. In Fig. 17 are shown the heating and cooling curve of N-28 containing: Cu, 4.98 per cent.; Mg, 2.41 per cent. On the up curve, the usual 520° C. arrest is noticed; on cooling, however, instead

of one, three arrests are noticed: at 502° C., at 478° C., and at 456° C. This cycle will repeat itself indefinitely, not only in this alloy but in others containing copper and magnesium, particularly when of rather high copper and magnesium content.

The structure of Fig. 20 was obtained in N-28 after the thermal analysis was completed and is characteristic; practically all of the Mg_2Si is surrounded completely by $CuAl_2$. Upon cooling, $CuAl_2$ separates at the first arrest (500° C.); at the second and third, Mg_2Si, and possibly some traces of Mg_4Al_3. These crystallize inside of the $CuAl_2$; the aluminum particles of the respective eutectics coalesce with the aluminum grains. Upon reheating this alloy, the surface of contact between Mg_2Si and aluminum is so slight that the melting of the eutectic, which should normally occur at the two lower cooling arrests, proceeds too slowly to give an arrest; and not until the protecting sheath of $CuAl_2$ melts as eutectic at the higher (520° C.) arrest does the Mg_2Si melt also. Those thermal arrests obtained around 500° C. are related to the formation of the various eutectics and do not have anything to do with the hardening of duralumin.

Conclusions Relative to Manufacture and Heat Treatment of Duralumin

It has been shown that when duralumin is rapidly cooled by quenching from temperatures between 250° and 520° C., and aged thereupon at temperatures from 0° to 200° C., the hardness and, at least at lower aging temperatures, the ductility increase. The actual values of hardness and ductility thus obtained depend on the quenching temperatures; they increase with that temperature up to about 520° C., corresponding to the increase of $CuAl_2$ in solid solution. At this temperature, any free $CuAl_2$ melts as a eutectic and the material is spoiled; this eutectic temperature, therefore, marks the upper limit of the useful quenching temperature range.

In order to develop the best mechanical properties by heat treatment, a quenching temperature should be used as near this as is possible without running risk of burning the metal by the melting of this eutectic. In practice, it should be possible to quench from temperatures between 510° and 515° C. The period of time at which sheet material should profitably be held at the quenching temperature lies between 10 and 20 min. Heavier sections, such as bars, might require more time at this temperature as the structure of such sections would be coarser and would require somewhat more time for the complete solution of the $CuAl_2$.

Quenching is best and most conveniently carried out in boiling water. The mechanical properties are better after quenching in hot than after quenching in cold water, and there is less danger of cracking due to cooling stresses.

The best temperature for subsequent aging depends on the mechanical properties that are desired. For most purposes it will be found best to age at 100° C. for about 5 to 6 days. The greater portion of the hardening effect takes place within this period. Such a treatment develops both high strength and high ductility. If a material having a higher proportional limit but lower ductility is desired, the material may be aged at higher temperatures up to 150° C. for from 2 to 4 days.

The authors' experience has not led them to recommend a different composition for duralumin than that in current use: Cu, 3 to 4.5 per cent.; Mg, 0.4 to 1.0 per cent.; Mn, 0 to 0.7 per cent.; 99-per-cent. Al, remainder.

It is believed that it would be of advantage to preheat the ingots for hot rolling to a somewhat higher temperature than is sometimes used. It would be desirable to preheat to 500° C. or as near to that temperature as the temperature uniformity of the furnace permitted; the free $CuAl_2$ would have better opportunity of going into solution at this temperature than at lower ones. Rolling, however, cannot be done at this temperature due to the eutectic melting of the Mg_2Si at 450° C. and consequent hot-shortness of the material. It might, therefore, be advisable to preheat to 500° C. but to roll at about 450°.

Summary and Conclusions

The heat treatment of alloys of the type of duralumin was investigated and the effect upon the mechanical properties observed of variations in the heat-treating conditions, such as quenching temperature, temperature of quenching bath and of aging or tempering, and time of aging. Conclusions are drawn relative to the best conditions for commercial heat-treating practice for this alloy. The temperature of quenching should not be above that of the $CuAl_2$—aluminum eutectic, which is usually about 520° C., but should be as near to this as possible without danger of eutectic melting. The pieces should be held at this temperature from 10 to 20 min. and quenched preferably in boiling water. The hardening, for most purposes, may best be produced by aging for about 5 days at 100° C.

A theory of the mechanism of hardening of duralumin during aging after quenching from higher temperatures was developed, which is based on the decreasing solubility of the compound $CuAl_2$ in solid solution in aluminum with decreasing temperatures from 520° to ordinary temperatures. It is believed that the precipitation of excess $CuAl_2$, which is suppressed by quenching, proceeds during aging, the precipitation taking place in very highly dispersed form. The hardening is due to the formation of this highly dispersed precipitate.

According to this theory, the hardening of duralumin during aging

or tempering after quenching presents a very close analogy to that of steel, and the evidence in support of the theory is of the same nature and of approximately the same competence as that in support of the prevailing theory of the hardening of steel.

DISCUSSION

ZAY JEFFRIES, Cleveland, Ohio (written discussion).—The autorsh conclude that there is a certain average size of precipitated $CuAl_2$ particle which produces maximum strength and hardness in duralumin; that when the size of particle is smaller or larger than this particular size the hardness decreases. The writer agrees with this conclusion, because it seems to be directly indicated by the facts.

Why does duralumin present this apparent discrepancy? Let us consider some physical aspects of the precipitation of $CuAl_2$ from a saturated solution on cooling. When a molecule of $CuAl_2$ is removed from the solvent, or matrix, and added to another group of $CuAl_2$ molecules, as is known to occur on slow cooling, the forces of adhesion between the $CuAl_2$ molecule and the solvent have been exceeded. Since a change in temperature only is sufficient to cause precipitation, it must also be sufficient to cause the loss of adhesion bonds between the excess $CuAl_2$ molecules and the solvent, or matrix. Lost adhesion bonds means loss of cohesion of the mass as a whole.

When duralumin is cooled from 500° in a furnace, globules of $CuAl_2$, large enough to be seen easily with a high-power microscope, are formed. There are, however, globules so small as to be hardly distinguishable, and others too small to be resolved are suggested by the non-uniformity of the surface appearance of the section. As the smallest globule of $CuAl_2$ resolvable with a high-power microscope contains about 2,000,000,000 molecules, it is evident that with rapid cooling submicroscopic particles of $CuAl_2$ must be present in large numbers; in fact, after quenching, the average size of particle must be submicroscopic. The whole phenomenon of aging must therefore involve changes that cannot be studied directly with a microscope.

We must also accept the proposition that the change in properties on aging are due to molecular changes within the metal; that those molecular arrangements are not possible in liquid air; that they take place slowly at ordinary temperature and more rapidly as the temperature is increased. We can visualize these molecular rearrangements best by assuming that the precipitation of $CuAl_2$, and segregation into particles, are two distinct steps. Immediately after quenching duralumin from 500°, the excess $CuAl_2$ is considered to be precipitated; some of it will have formed into small particles, and some will be precipitated as single molecules which have little or no adhesion with the particles of the matrix.

This condition produces the low mechanical cohesion observed in duralumin after quenching and before aging. The increase in cohesion of the whole mass could be brought about by the agglomeration of these precipitated molecules of $CuAl_2$. In the first place, the particles of the matrix would establish cohesion bonds with one another in the space formerly occupied by a $CuAl_2$ molecule. This would increase the cohesion of the matrix, then the small globule, made up of many $CuAl_2$ molecules, would acquire its own specific cohesion.

Having thus produced increased cohesion of the matrix and the $CuAl_2$ particles, we have only to account for the observed increased cohesion or hardness of aged duralumin.

As some $CuAl_2$ is soluble in the matrix at room temperature, it is only the excess that can form into minute globules. The presence of a globule of $CuAl_2$ acts as a center of crystallization, and hence easily attracts to itself the adjacent excess $CuAl_2$ molecules in the matrix and impoverishes the matrix at the boundary. This accomplishes two things; it facilitates migration of $CuAl_2$ toward the globule by forces of diffusion and it reduces the number of $CuAl_2$ molecules in the matrix at the boundary with the globule to normal saturation, which is the condition for maximum adhesion between $CuAl_2$ and the matrix. Thus the strong adhesion bond between these two substances is established. It is probable that the concentration of a saturated solution of $CuAl_2$ in aluminum in the absence of $CuAl_2$ nuclei is greater than when these nuclei are present. It is also probable that the actual boundary between a $CuAl_2$ particle and the matrix is an amorphous solution of $CuAl_2$ in aluminum.

According to the above, the reason that maximum diffusion does not produce maximum cohesion is that the adhesion bonds between the excess $CuAl_2$ molecules and the matrix are not strong, and the spaces they occupy might act as voids in affecting cohesion. Aging removes the voids from the matrix, thus increasing its cohesion; it establishes cohesion in the newly formed $CuAl_2$ globules, and adhesion between these and the matrix. If the particles of $CuAl_2$ continue to increase in size beyond a certain average, and decrease in number, as in prolonged aging, at 200°, the cohesion decreases.

The formation of cohesion and adhesion bonds between the atoms and molecules in duralumin at room temperatures might be questioned. If we press two pieces together and allow them to remain at ordinary temperatures for long periods of time, we cannot produce such results. No doubt the absorption phenomenon militates against this low temperature welding,[18] as do unclean surfaces due to oxidation. The formation of

[18] Langmuir: *Jnl.*, Amer. Chem. Soc. (1916) **38**, 2221; (1917) **39**, 1848; (1919) **41**, 868.

cohesive masses of metal at ordinary temperature by electro-deposition teaches us that high temperature is not necessary for the formation of cohesive bonds. The interior of a mass of duralumin should be free from adsorption and oxidation, hence the atoms and molecules would be free to form bonds with one another at temperatures much below that of welding. It should be kept in mind that welding is accomplished at high temperatures in spite of the retarding influences of adsorption and oxidation.

The heat evolution observed at about 260° might well be due to a rapid crystallization of $CuAl_2$ rather than the mere precipitation. The fact that rupture takes place through the grains is evidence that, whatever changes go on within the alloy, those that affect the physical properties must be intracrystalline.

Other alloys will, no doubt, show similar changes in properties when studied in the proper temperature range. Future investigations of alloys at various temperatures must form the basis for a more complete and modified interpretation of the new and old facts observed in connection with the phenomenon called aging. Quantitative evidence must be introduced as soon as facts permit. Aging experiments on duralumin extending over a period of many years will be interesting with respect to the relations between the changes in properties and the engineering uses. It is obvious that the material cannot be used at 200° for a long time without changing markedly in properties. What is the maximum temperature that will permit so little change on extended aging of duralumin that it may be used with safety at that temperature? A study of this question is necessary in order to change the specific composition and heat treatment of the alloy to meet certain engineering requirements.

P. D. Merica (author's reply to discussion).—We are greatly interested in Doctor Jeffries' explanation of the increased tenacity of a colloidal solution of $CuAl_2$ in aluminum over that of a solution of molecular dispersion. It is only by searching out the molecular mechanism of changes of this character in alloys that we shall arrive at the ultimate truth regarding their nature. Based upon thermodynamical laws, which are accurate enough but rather barren of suggestion regarding molecular dynamics its methods in reaching beyond this firm foundation are rather those of "main strength and awkwardness" and there is unfortunately little of modern molecular theory available in the proper form for our aid. It is to be hoped that researches into the structure of solids with the aid of the X-ray diffraction microscope will bring much needed light into these matters.

Water and Chlorides in Cement Copper Briquettes

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(Chicago Meeting, September, 1919)

ALTHOUGH the subject matter contained in this paper is presented under a new title, its writing was induced by the work of S. Skowronski and K. W. McComas.[1] A discussion of the latter is here combined with the presentation of new and independent data.

The physical constants quoted by the authors of that paper, such as melting and boiling points, as also the chemical reactions of the substances involved, are so well established that the numerous confirmatory experiments and their application to metallurgical conditions leave little or no room for criticisms. On the contrary, they will greatly aid to dispel any lingering skepticism as to possible considerable losses of copper accruing when the metal is melted in the presence of its own and, probably, other chlorides and when no provision is made for the recovery of volatile products. Exception may be taken, to some degree, to that part of the work under the caption Melting Drillings of Copper Mixed with Sodium Chloride. These experiments should have been extended in order to make the implied reactions clear and the results convincing. The latter are stated to be, "that when sodium chloride is present above certain minimum quantity relative to copper some of it is found to volatilize in the melt while another part reacts with the metallic copper to produce the volatile cuprous chloride, and that when smaller quantities of sodium chloride are present the reaction is complete and all chlorine is found to have volatilized as cuprous chloride." Metallic copper and sodium chloride are mentioned as the sole reagents in this chemical process, acting, according to the authors, in a neutral atmosphere of carbon dioxide. The chemist, quite naturally, will inquire into the formula according to which that reaction takes place and will find that it presents itself as follows:

$$2Cu + 2NaCl = 2Na + Cu_2Cl_2$$

It would appear that the truth of this formula will be challenged and a more rational explanation of the reaction sought. Apparently, carbon dioxide is neutral relative to metallic copper in its molten state; whether it remains neutral in the presence of sodium chloride is quite another

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[1] Volatilization of Cuprous Chloride on Melting Copper Containing Chlorine *Trans.* (1919) **60**, 354.

question. Does it not at that high temperature become an oxidizer and do not the conditions of the reaction change to those expressed in the following formula?

$$2Cu + 2NaCl + 2CO_2 = Na_2CO_3 + CO + Cu_2Cl_2$$

Nor has there been any mention made, as an element in the reaction, of the substance and relatively large surface of the boat in which the melt was made. Be it silica or alumina, the sodium, once oxidized, will readily combine with either to form sodium silicate or sodium aluminate, making the chlorine available to form cuprous chloride. It is most likely that the reaction takes place according to the last statements. In short, the reaction between metallic copper and such stable chlorides as those of sodium and calcium without the presence of a third, or acid principal, would appear improbable. The copper losses due to such foreign chlorides in metallurgical practice would, therefore, largely depend on how readily the acid material is supplied and brought into contact with the chloride; furnace gases would always supply oxygen or carbon dioxide. The final question is, would a thoroughly basic condition of the fluxes in the melting furnace prevent the formation of cuprous chloride?

Presence of Water in Briquettes.—Some years ago copper cement briquettes became a problem in sampling. In a test demonstrating that drilling the briquettes was perfectly feasible, every tenth piece was taken for that purpose. Drilling was performed according to a templet fitting the flat side of the object and laid out in 1-in. (2.5 cm.) square sections, each briquette receiving one drill hole. There was very little trouble on account of chipping on the exit of the drill; although occasionally a small piece became detached, it could readily be picked from the drillings, these being pulverulent. Cracking of the briquettes was rare. It was soon discovered that the briquettes contained considerable moisture but to determine this in the drilled sample was deemed inadvisable.

Spontaneous Oxidation or Ignition of Briquettes.—The drying oven had been employed in drying converter copper slabs, which required a temperature of about 400° F. (204° C.). When the briquettes were removed after having been exposed to a recorded temperature of about 200° F. (93° C.) their weight had increased; their darkened appearance made it evident that oxidation had taken place. As a consequence, it was decided to reduce the drying temperature to 180° F. (82° C.) and to lengthen the time of exposure to the heat. Still there would be, occasionally, a repetition of spontaneous oxidation and the briquettes would come out overweight. This in itself, however, was not considered objectionable; provided that there were no valuable losses or that these were negligible, correct results could be as well obtained as with the sample in which the moisture was properly determined. For example, if a sample gained 7 per cent. of its original weight there would be a

corresponding reduction in the assay results; but these could be properly applied to the lot by increasing the original lot weight by 7 per cent.

Presence of Chlorides in Briquettes.—The presence of chlorine in these briquettes was known and some fumes and certain poignant odors were emitted from the lots that were oxidized. It had also been observed that the oxidized briquettes had attained a higher temperature than that observed in the atmosphere of the drying oven. This temperature of the briquettes was never determined, but it seems certain that it did not reach a red heat, as no glow was ever observed. The interior of the oven was carefully examined. Its wall, ceiling, and doors consisted entirely of iron plates; the latter showed principally a thin sooty covering but in places it appeared mixed with a yellow substance. At one time when the oven was not in operation and, evidently, a little water had percolated through a joint in the ceiling, there was a place with a clean looking bluish accumulation; this was scraped off carefully and taken for a sample. Scrapings from the walls were taken for a second sample. The first will hereafter be designated as the ceiling condensation and the latter as the wall condensation. There can be no doubt but that these samples contained some of the condensed fumes that had been emitted by the briquettes, overheated by spontaneous ignition.

In Tables 1 and 2 are given the analyses of the briquettes, which were quite uniform in composition, and of the condensed fumes' samples. By simple arithmetical calculations are found the contents per unit of copper

TABLE 1.—*Analyses of Cement Copper Briquettes and Condensed Fumes*

Material	Copper, Per Cent.	Chlorine, Per Cent.	Arsenic, Per Cent.	Silver, Ounces	Gold, Ounces	Iron, Per Cent.	Sulfur, Per Cent.	± Weight in Drying, Per Cent.
Cement copper, dried....	81.15	1.081	0.706	52.35	0.015	3.29	1.803	−0.376
Cement copper, oxidized	76.44	0.960	0.679	47.82	0.015	3.64	0.510	+8.910
Ceiling condensation...	14.74	8.100	1.800	144.12	0.040			
Wall condensation.....	1.48	0.970	0.550					

TABLE 2.—*Analyses of Cement Copper Briquettes and Condensed Fumes*

Material	Copper, Per Cent.	Chlorine, Per Cent.	Arsenic, Per Cent.	Silver, Ounces	Gold, Ounces
Contents per Unit of Copper					
Cement copper, dried.....	1	0.0133	0.00870	0.645	0.000186
Ceiling condensation.....	1	0.5490	0.122	9.76	0.00271
Wall condensation.....	1	0.6560	0.37		
Ratio of Elements Volatilised and Condensed					
Ceiling condensation.....	1	.....	14.04	15.16	14.60
Wall condensation.....	1	.....	42.53		

and from these the ratio of volatilization and condensation, which figures are also incorporated in the table. It will be noticed that in the wall condensation the precious metals were not determined, due to the smallness of the sample.

In Table 3 are given a few physical data extracted from Moissan's "Traité de Chimie Minérale," Paris, 1906. The chlorides of silver and gold

TABLE 3.—*Melting Point, Boiling Point, and Volatility of Some Chlorides*

Chloride	Fusing Point, Degrees C.	Boiling Point, Degrees C.	Volatile at Degrees C.
Cu_2Cl_2	434	934–1032	
$AsCl_3$	−16	130–160	Below boiling point
AgCl	487–490		Begins at 260
AuCl	288		Begins at 180

having no boiling point, it is evident that they volatilize, or sublime, without boiling, at least to a certain extent; or that they become dissociated at higher temperatures. Apparently arsenious chloride is the most volatile and cuprous chloride the least volatile of the group in question. These facts explain the greater relative volatility of the chlorides of arsenic, silver, and gold than of the cuprous chloride. The greater quantity of arsenic in the wall condensation relative to copper than in the ceiling condensation is also readily explained by the facts that the briquettes were at a considerably greater distance from the walls than from the ceiling; therefore, the less volatile chloride would condense to a greater degree at the nearest surface, while the more volatile would reach more distant points.

It is impossible to state in what combination the chlorine was originally present in the briquettes. If the volatilized and condensed chlorides did not preëxist in the briquettes, their formation under the prevailing temperature would be somewhat difficult to explain, say, by the presence of sodium chloride. Ferrous chloride under the influence of oxidation might bring about such reactions and the actual presence of iron in the briquettes makes that explanation plausible.

Under the described conditions of the technical operations it was impossible to conduct quantitative tests as to actual losses, but it may be stated, with quite a fair degree of confidence, that they were negligible, as judged by the small quantity of condensed material and the great weight of briquettes treated. However, all this occurred at comparatively low temperatures and justifies the inference that, at the temperature of the copper melting furnaces, losses in copper will be serious and that of the precious metals relatively still greater. The presence of arsenic, taking up its full share of the chlorine, will be somewhat of a palliative against greater losses of the more valuable metals.

Foretelling Losses Quantitatively.—From what has been demonstrated by the analytical data presented, it becomes evident that the action of chlorine, or the chlorides, in the melting furnace on argentiferous auriferous copper, with the usual contingent of various impurities, becomes a very complicated chemical problem, making it practically impossible to foretell quantitatively the losses of valuable metals.

The problem of melting cathode copper in contact with chlorides would appear a more simple problem, yet there is a great probability of conditions arising that would bring about great variations of copper losses, even with an invariable quantity of chlorine present. It is not plausible that the acidity or basicity of the fluxes, be these intentional or accidental, will not influence the reaction between foreign chlorides and metallic copper.

Judging by qualitative tests made, it would appear, with much probability, that greatly differing quantitative results will be obtained in the distilling tube and boat under conditions expressed, as examples, in the following formulas:

$$x\,Cu + y\,NaCl = ? \quad (1)$$
$$x\,Cu + y\,NaCl + z\,SiO_2 = ? \quad (2)$$
$$x\,Cu + y\,NaCl + z\,CaO = ? \quad (3)$$

In tests according to these formulas, temperature, time and atmosphere would be assumed to be invariable.

Electrolytic Zinc*

BY C. A. HANSEN,† SALT LAKE CITY, UTAH

(Chicago Meeting, September, 1919)

Roasting Ferruginous Zinc-sulfide Ores

In 1912, Mr. J. B. Keating was developing an electrolytic-zinc process for application to the ores of the Bully Hill mines of the General Electric Co. These ores consist of blende and pyrite so finely crystallized and so intimately mixed that no mechanical separation of the individual minerals had been found possible. The ore was reduced to about 60 mesh and roasted in a hand-rabbled reverberatory furnace preparatory to leaching with sulfuric acid. The extractions obtained were quite irregular, varying from a minimum of about 70 per cent. to a maximum of about 90 per cent. This irregularity led to the construction of a small electrically heated roasting furnace, and to the study of roasting under definitely controllable conditions. From time to time, these studies have been extended to other ores. Several commercial-plant operators profess to have gained useful information from the results of these studies and it is hoped that their usefulness may be extended by this publication.

Experimental Electric Roasting Furnace

The furnace used for experimental work is shown in Fig. 1. One fireclay sagger, or pot, was set within another and the space between the two filled with Silox heat insulation. The hearth is a cast-iron plate with an imbedded ribbon of nichrome wire; this wire heater is connected to a potential regulator, which permits a very close voltage control. A mechanically driven arm is fitted with rabble blades so arranged that a uniformly thick ore bed may be maintained indefinitely. This arm is usually driven at about one revolution per minute but its speed of rotation can be varied as desired. Compressed air is led into the furnace through a meter, and it was found necessary to preheat the air in order to secure the definitely isothermal conditions sought.

With this arrangement, it is possible to maintain any desired temperature constant within about 5° C. for any desired length of time and to

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* Second paper on this subject. The first, dealing with electrolysis of zinc sulfate solutions, appeared in *Trans.* (1919) 60.

† Metallurgist, General Elec. Co., Research Laboratory.

maintain temperature alike in the hearth, in the ore bed, and in the space above the ore bed. Heraous (*Pt-Pt-Rh*) thermocouples were kept in the hearth, in the space above the ore bed, and in the air feed-pipe and were connected to recording instruments. The couples were frequently calibrated, and considerable pretense to accuracy is claimed for the temperatures recorded in connection with this work. Gas samples were taken at the air outlet of the furnace, and calcine samples were taken at frequent intervals.

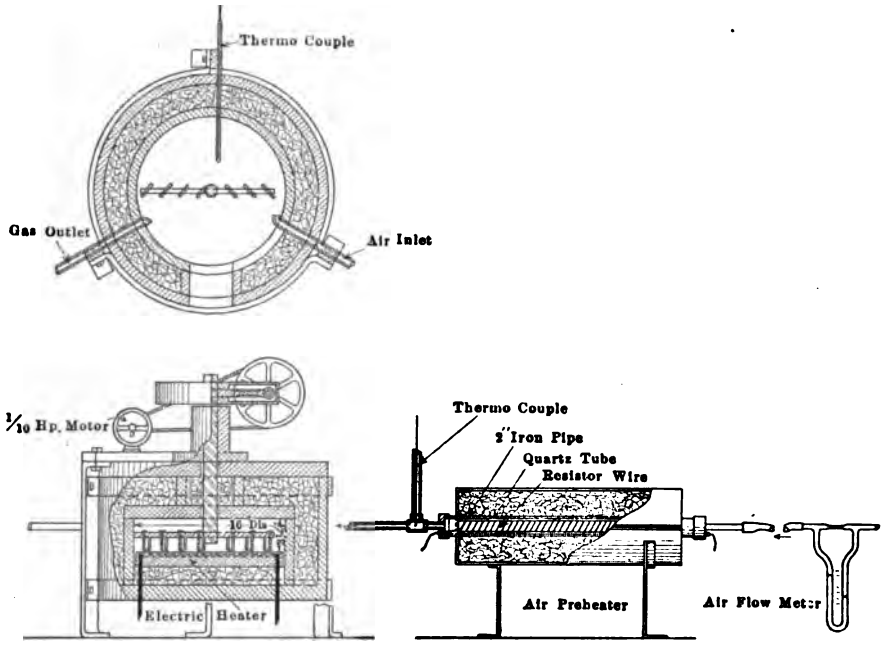

FIG. 1.

ANALYTICAL METHODS

Sulfur-dioxide concentrations in the roaster gas were determined by absorption in standard iodine solution and titration with thiosulfate. Water-soluble zinc in the calcines (zinc sulfate) was determined by bringing to a boil 5 gm. samples of calcine together with 200 c.c. of water, and by titration of filtered off solution with ferrocyanide. Total soluble zinc was determined by boiling, for 5 min., 1 gm. samples of pulverized calcines together with 0.75 gm. sulfuric acid and 100 c.c. water. (This gives a solution only faintly acid; the test is wholly an arbitrary one that has been found to give consistent results.) The filtered solution is titrated with ferrocyanide after the usual fashion.

Insoluble zinc is determined in the residuum from the soluble zinc determination, and the extractions reported refer to soluble zinc/soluble zinc plus insoluble zinc.

While this method of determining extraction is more tedious than one involving the determination of the total zinc directly, it leads to rather more consistent results and also to the direct determination of the insoluble zinc, which, after all, is the most important of determinations.

Sources and Nature of Ores Tested

Bully Hill, Bully Hill Copper Mining Co., Shasta Co., Calif., is an unconcentrated ore, massive sulfide. The minerals are apparently sphalerite and pyrite and are so finely crystallized, and finely intermixed as practically to defy separation. The gangue material is mainly barium sulfate. Butte Superior, Butte Superior Copper Mining Co., Butte, Mont., flotation concentrates obtained in 1912 were apparently a mixture of pure sphalerite and pyrite. Daly Judge, Judge Mining & Smelting Co., Park City, Utah, table and flotation concentrates are pure sphalerite and pyrite, quite coarsely crystallized. Individual zinc crystals contain no iron or lead and individual pyrite crystals contain no zinc. Broken Hill, Amalgamated Zinc (DeBavay's) Ltd., Broken Hill, Australia, flotation concentrates have iron combined with zinc as ZnS:FeS. Frisco, Federal mines, Coeur d'Alenes, Ida., 1916, apparently a flotation concentrate in which iron is apparently combined with zinc as FeS:ZnS.

Analyses of Ores Tested

	Bully Hill, Per Cent.	Butte Superior, Per Cent.	Broken Hill, Per Cent.	Daly Judge, Per Cent.	Frisco, Per Cent.
Zinc	23.80	50.70	48.80	47.70	37.97
Copper	1.85	0.57	0.33	1.12	0.03
Iron	16.60	2.30	8.55	4.50	7.90
Sulfur	31.50	27.60	27.30	27.00	24.00
Cadmium	(0.30)	(tr.)	0.052	(0.31)	0.23
Lead	(tr.)	2.79	6.12	2.19	13.56
Silica	(6.30)	19.30	1.75	(6.70)	11.04
Lime	(2.31)	.....	0.50	(4.95)	0.25
Magnesia	(2.86)	.....	0.06	.....	0.46
Alumina	(8.26)	(1.56)	0.56	1.80	2.07
Barites	(2.94)	.....	....	.....	....
MnO	(0.60)	1.50	1.33	0.67	0.76
Silver, ounces	(1.00)	26.00	7.80	12.20	4.60
Gold, ounce	(0.03)	0.046	0.01	0.02	0.005

Figures given in parentheses refer to analyses of samples other than those specifically tested.

SCREEN ANALYSES

	Bully Hill	Broken Hill	Daly Judge	Frisco
Plus 20 mesh	0.0	0.0	0.2	0.6
20–40	0.0	11.0	22.4	18.7
40–60	0.0	19.4	19.4	12.8
60–80	5.6	22.5	21.4	20.6
80–100	11.6	7.5	6.1	5.9
100–150	11.2	44.0*	30.6*	38.3*
150–200	15.2			
-200	56.0			

* Refers to minus 100 mesh.

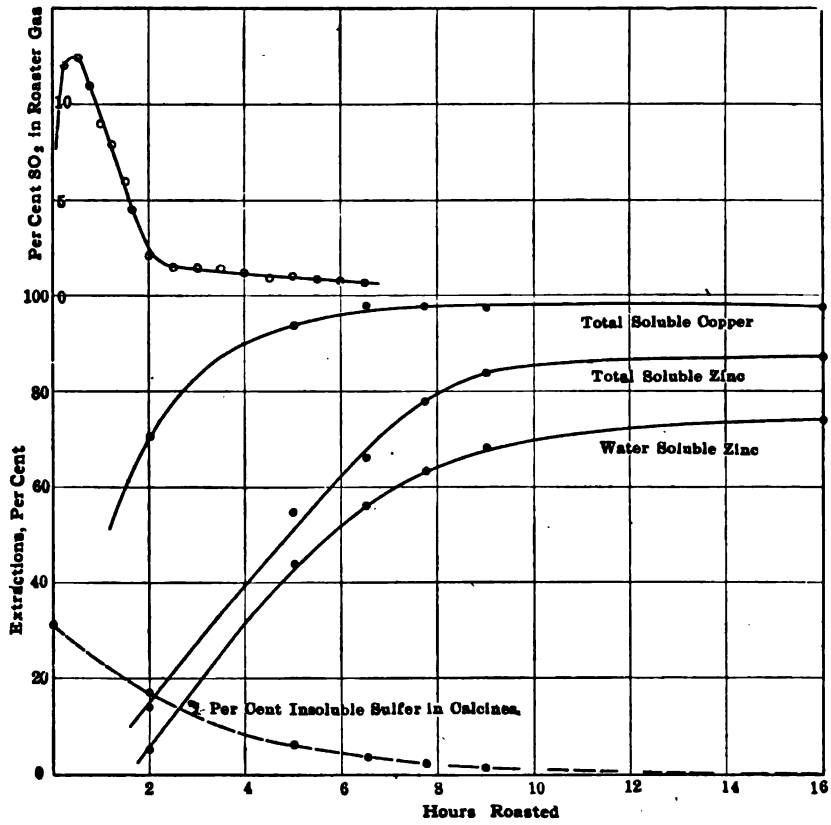

FIG. 2.—ROASTING BULLY HILL ORE, 575° C.; 7 LB. ORE TO 16-IN. HEARTH. 1.15 CU. FT. AIR PER MIN. PREHEAT, 330° C.

No screen analysis record of the Butte Superior concentrate is at hand. The material was very fine, most of it probably passing through a 100-mesh screen.

Results of Experimental Roasting in Electrically Heated Roaster

Bully Hill Ore.—This material was roasted isothermally at 425°, 450°, 475° C. and so on at 25° intervals up to the limit of the roaster,

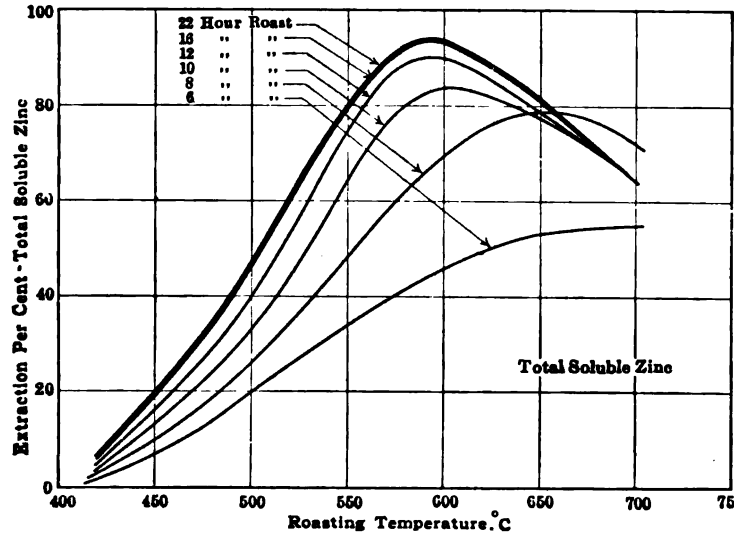

Fig. 3.—Bully Hill ore isothermally roasted; 7 lb. ore to 16-in. hearth. 1.15 cu. ft. air per min.

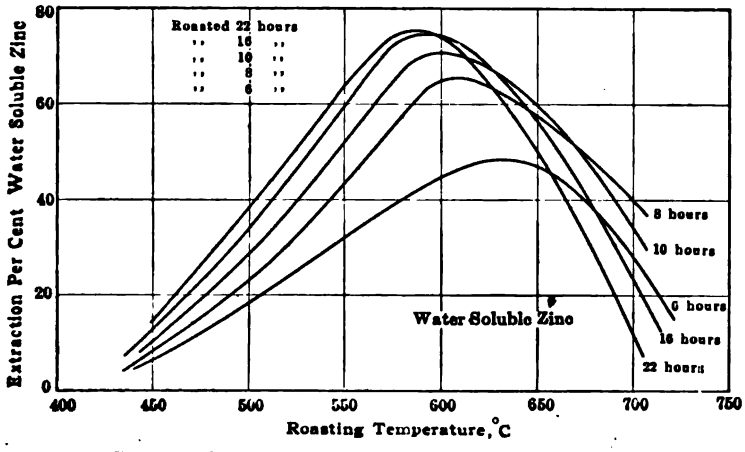

Fig. 4.—Bully Hill ore isothermally roasted.

700° C. Fig. 2 shows the results obtained at the optimum tamparature 575° C. Similar plots were made for each roasting experiment, and the results, in slightly idealized form, are shown in Fig. 3. The summarized data relative to the formation and decomposition of zinc sulfate are given in Fig. 4.

The sulfur-dioxide concentration curve in Fig. 2 shows quite markedly the flashing off of the pyrite sulfur and that practically all of such sulfur is oxidized before the zinc sulfide is appreciably reacted upon. No water-soluble zinc sulfate is formed until the sulfur-dioxide concentration falls below some 2–3 per cent., but beyond the time at which the sulfur-dioxide concentration reaches this low value practically all of the zinc sulfide oxidized was converted to zinc sulfate. Thus between the second and sixteenth hour, the gain in total soluble zinc was 73 per cent. and the gain in water-soluble zinc was 69 per cent.

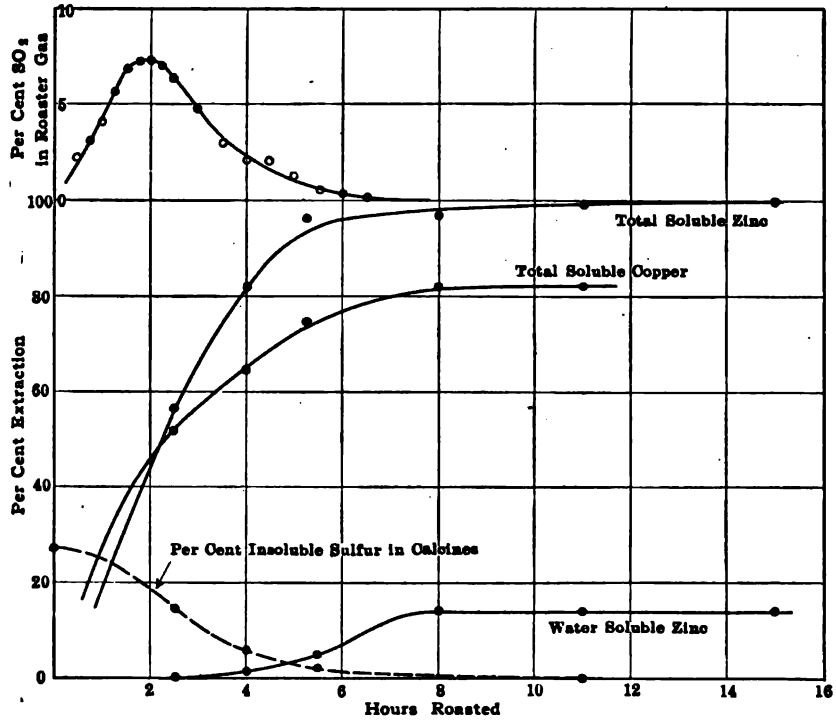

FIG. 5.—BUTTE SUPERIOR FLOTATION CONCENTRATES ROASTED AT 575° C.

The effect of varying the amount of air fed to the roaster is indicated by the following:

Cubic feet of air per minute	1.15	0.86	0.56
Pounds of ore on hearth	7.0	7.0	7.0
Temperature, degrees C.	575	575	575
Hours roasted	12.00	14.00	15.00
Zinc extraction, per cent			
Total soluble	87.00	87.00	87.00
Water soluble	76.00	48.00	16.00

The formation of zinc sulfate is important in so far as water-soluble sulfate in the calcines reduces the amount of acid required from outside

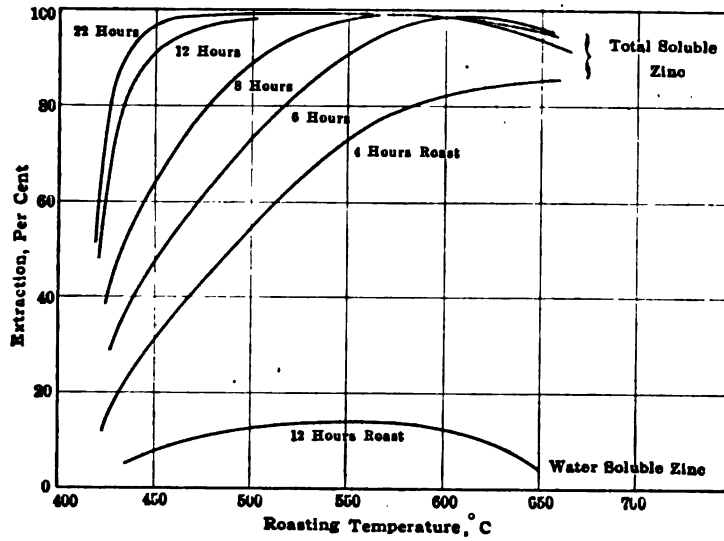

FIG. 6.—BUTTE SUPERIOR FLOTATION CONCENTRATES ISOTHERMALLY ROASTED.

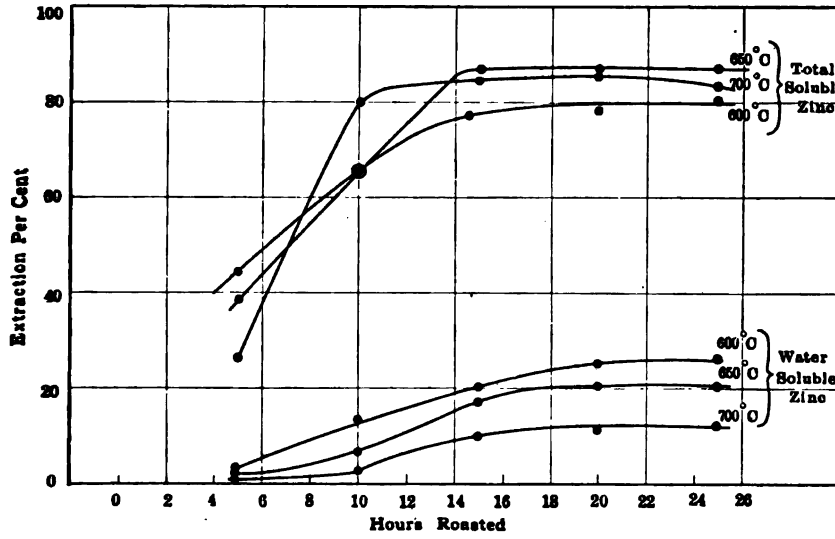

FIG. 7.—BROKEN HILL CONCENTRATES ISOTHERMALLY ROASTED.

sources for the leaching operations. Ordinarily, if the calcines contain 3 to 4 per cent. of water-soluble zinc, based on the calcines weight, the zinc plant becomes self-supporting in its acid requirements.

Butte Superior Concentrates.—Fig. 5 shows the behavior of finely divided high-grade zinc concentrates roasted at 575° C. The sulfur-

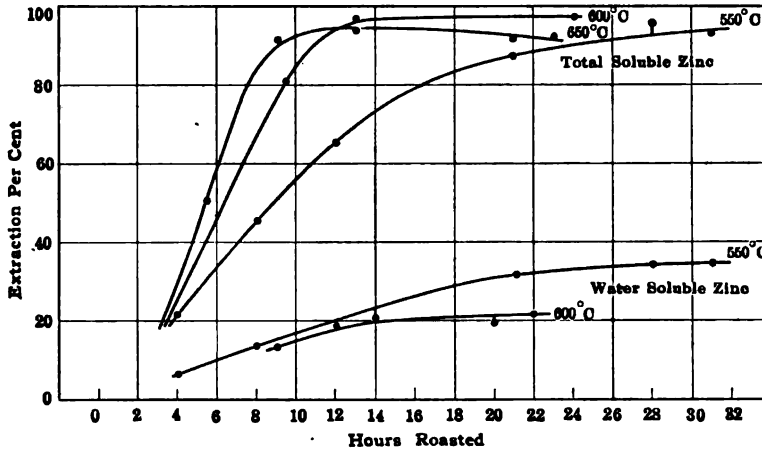

FIG. 8.—DALY-JUDGE CONCENTRATES ISOTHERMALLY ROASTED.

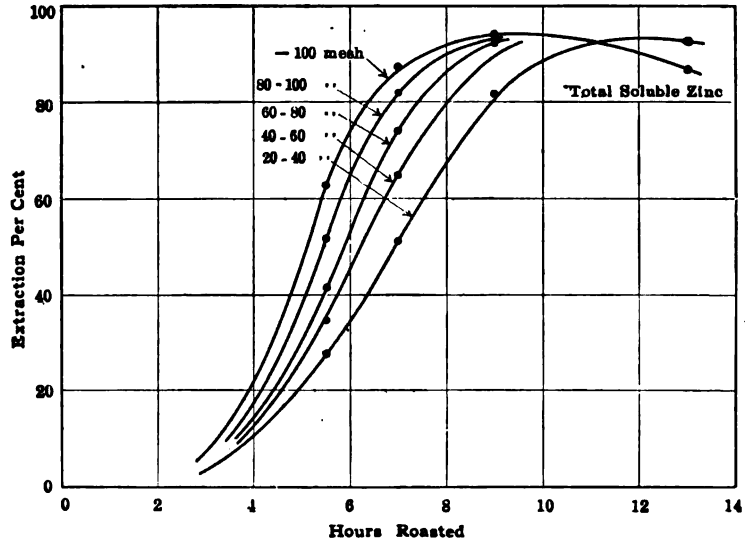

FIG. 9.—DALY-JUDGE CONCENTRATES ROASTED ISOTHERMALLY AT 650° C. EFFECT OF SCREEN SIZE.

dioxide concentration curve shows no flashing off of large quantities of pyrite sulfur. The oxidation of zinc sulfide begins almost immediately but there is no formation of sulfate until the sulfur-dioxide concentra-

tion has fallen to about 2 per cent.; beyond this point there is a gain of 14 per cent. water-soluble zinc, as compared with a gain of 17 per cent. in total soluble zinc.

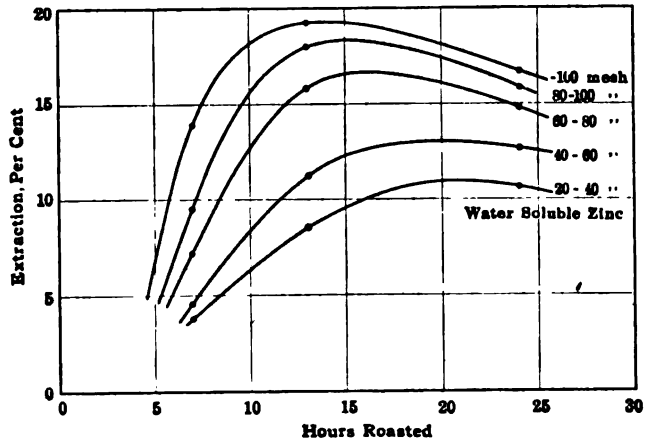

FIG. 10.—DALY-JUDGE CONCENTRATES ROASTED ISOTHERMALLY AT 650° C.

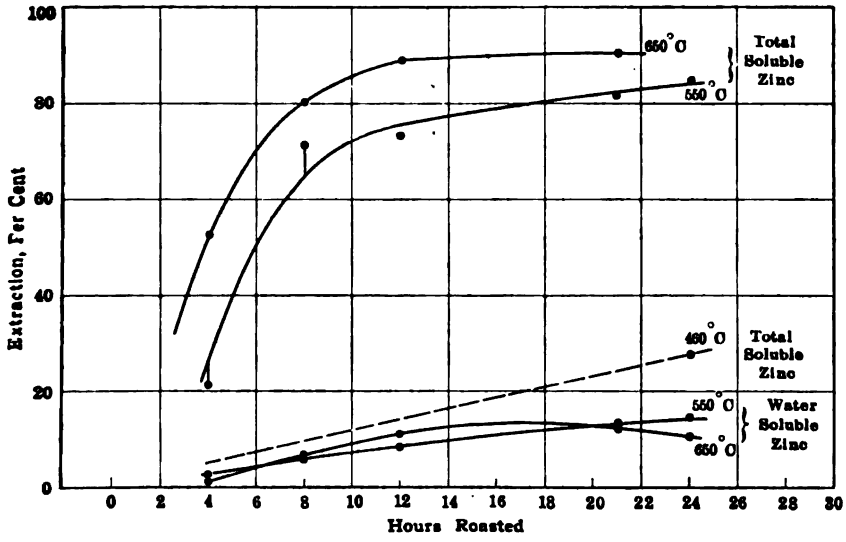

FIG. 11.—FRISCO (COEUR D'ALENES) CONCENTRATES ROASTED ISOTHERMALLY.

Fig. 6 summarizes very broadly the results obtained during four experimental roasts at 450°, 500°, 575°, and 650° C. It is curious to note that 22 hr. roasting at 450° C. rendered 97.6 per cent. of the zinc

soluble. The calcines obtained from the 450° roast accounted for all but 0.75 per cent. of the original silver content. The calcines obtained at 650° C. showed a loss of 13.9 per cent. of the original silver content. The writer understands that the roasting of similar concentrates at Bartlesville led to a silver loss of 26 per cent. The roasting at Bartlesville was accomplished in Zellweger furnaces where the concentrates were exposed 24 hr. to temperatures above 900° C. No pretense is made that the above silver determinations are more than merely indicative of the relations between silver loss and roasting temperature.

Broken Hill Concentrates.—Fig. 7 summarizes the results obtained in roasting this material at 600°, 650°, and 700° C. It is apparent that the coarser screen size leads to a longer roasting period. In spite of the low iron content of these concentrates, we could not obtain extractions higher than 87 to 88 per cent. Similar concentrates roasted at high temperatures in Matthiessen Hegeler kilns yielded 87 per cent. extractions; roasted in a hand-rabbled reverberatory at high temperatures and at low temperatures also yielded 87 to 88 per cent. extractions. It appears that the zinc is combined with iron in the original mineral and that no manner of straight roasting will serve to break up the combination. This behavior is thoroughly characteristic of several isomorphous zinc-iron minerals (marmatites) with which we have experimented.

Daly Judge Concentrates.—Fig. 8 summarizes the results obtained in roasting this material at 550°, 600°, and 650° C., while Fig. 9 indicates the effect of screen size upon roasting rates. There is an excellent indication that in roasting a mixture of variously sized ore particles to secure maximum extraction for the mixture the fines will be over roasted. An interesting relation between screen size and the formation of zinc sulfate is brought out in Fig. 10.

Frisco Concentrates.—Fig. 11 summarizes the results obtained in roasting this material at 460°, 550°, and 650° C. This concentrate strongly resembles the Broken Hill concentrate in appearance and in its behavior in the roaster.

Roasting in a Hand-rabbled Reverberatory Furnace

The reverberatory roaster at Bully Hill had a hearth 8 ft. (2.4 m.) wide by 13 ft. (3.9 m.) long and was divided into two 4-ft. strips by a vertical partition wall. Ore was fed in periodically at one end of the two hearth strips, and periodically moved forward toward the discharge end. At the discharge end was placed a small combustion chamber into which oil was injected with steam. Roasting was carried on continuously and the following data are characteristic of continuous operating conditions.

Bully Hill Ore	Reverberatory	Electric
Temperature, degrees C	550–600	575
Pounds roasted per sq. ft. per 24 hr	12.50	12.20
Zinc extraction, total per cent.		
2 hr. roast	17.90	14.20
4 hr. roast	62.90	39.50
6 hr. roast	83.60	62.00
8 hr. roast	84.40	80.00
10 hr. roast	86.00	87.00
Zinc extraction, water per cent.		
2 hr. roast	10.70	5.00
4 hr. roast	30.30	30.50
6 hr. roast	36.80	52.00
8 hr. roast	32.00	63.50
10 hr. roast	41.40	70.40
Zinc in feed, per cent	27.22	23.80
Iron in feed, per cent	15.00	16.60

It should be noted that definite time samples are hard to get out of the reverberatory, and that the amount of water-soluble zinc obtained in the electric roaster could be controlled through control of air volume. At the time the above work was done in the reverberatory furnace, every endeavor was made to secure maximum oxidation to sulfate. The comparison then covers maximum possible water-soluble zinc sulfate for the two furnaces.

Broken Hill Concentrates	Reverberatory		Electric
Temperature (gas), degrees C.			
Cold end of furnace	605	808	650
	635	817	
	705	820	
	705	828	
Hot end of furnace	715	840	650
Average temperature, degrees C	713	821	650
Zinc extractions, total per cent.			
8 hr. roast	59.30	57.90	55.60
12 hr. roast	67.50	79.10	76.00
16 hr. roast	83.50	82.90	87.50
20 hr. roast	86.40	87.50	87.00
24 hr. roast	88.60	87.50	87.50
Per cent. water-soluble zinc in calcines.			
8 hr. roast	1.25	1.10	1.30
12 hr. roast	2.25	1.05	4.80
16 hr. roast	3.70	0.60	7.80
20 hr. roast	3.95	0.40	9.65
24 hr. roast	3.95	0.30	9.65
Pounds roasted per sq. ft. per 24 hr.			
24 hr. roast	14.4	14.4	5.80

It is apparent that in these two instances, the only instances where a direct comparison between the electric roaster and the reverberatory is possible from the data at hand, the two furnaces yielded practically identical extractions and that time factors for the two furnaces are at least comparable. The reverberatory furnace was rabbled with hand rakes about as frequently as a man could cover the hearth.

Roasting in Wedge Furnaces

When the first electrolytic-zinc plant, that at Trail, B. C., was built, practically no zinc ores had been roasted in the Wedge type of furnace (including the similar McDougal, Herreschoff, and Skinner designs) so far as the writer can learn. However, a Wedge roaster had been set up and operated in Philadelphia in connection with the manufacture of lithopone, but little information could be obtained relative to its performance. The general practice had apparently developed along the line of long-period roasting at relatively high temperature, Matthiessen-Hegeler, Zellweger, and other types of straight-line furnace types being used almost exclusively.

The electrolytic-zinc process was developed primarily to treat the western low-grade zinc ores and concentrates. As it is essential, to secure good extraction from low-grade concentrates containing considerable iron, to keep the temperatures in the roaster reasonably low—around 600° C.—it was thought that the Wedge furnace type could be adapted for this purpose. Since this time, Wedge furnaces have been operated continuously at temperatures approaching 800° C. but this appears to be about the limit, for the maintenance costs become almost prohibitive and frequent service interruptions are caused by the need for repairs. Temperatures considerably above 800° C. are commonly used in roasting for the retort—probably in order to break up the sulfates formed during the earlier stages of the roasting period—and it is probable that the aversion of the retort smelter toward the Wedge furnace type is more or less well founded.

For low-temperature roasting, the Wedge furnace promised economies in lower first cost, lower labor costs, and lower fuel consumptions as compared with the straight-line furnace types, and further incentive to its selection rested in the fact that the Western smelters were most familiar with the type. In any case, each electrolytic plant in the West independently selected the Wedge type of roaster but no published information is available regarding either practice or performance of the roasting equipment at these plants other than the brief statement made by E. H. Hamilton[1] to the effect that the Trail furnaces were treating 50 tons each per day.

[1] *Trans.* Amer. Electrochem. Soc. (1917) **32**, 317.

It is unfortunate that the entire period of operation of the electrolytic-zinc plants has been overlapped by the war period of abnormal cost and price conditions. Under these conditions, coupled with the fact that a completely new practice had to be developed throughout the zinc plant, the cost of the zinc available in the calcines has not been, by any means, the major item in the cost of producing electrolytic zinc. Almost any sort of roasting practice led to fair recoveries. Improvement in roasting practice could only lead to somewhat better recoveries of zinc and therefore only to the reduction of a minor cost item. Consequently, less attention has been given the roasting practice than would characterize practice in normal times. This undeveloped state of the roaster practice has unquestionably led to a reluctance to publish accounts of the roasting work already done, a reluctance that is shared by the writer.

All the operating electrolytic-zinc plants are dealing with zinc materials containing important quantities of lead, copper, silver, and gold, which must be recovered by smelting methods from the zinc-plant residues. As the zinc extraction is improved by improvements in roasting practice, the residues will decrease in weight and less penalty will be exacted by the smelter for zinc obtained in them. The savings accruing to a better roaster practice in these respects is quite as important as the direct additional saving of zinc. That which follows in regard to the operation of the Wedge roaster at the Judge zinc plant may properly be considered a mere teething experience but it seems to point the way toward some of the possible improvements in practice.

Wedge Furnace Roasting of Judge M. & S. Co., February–April, 1917

The primary values in the ores of the Judge mines are lead and silver. The ores, however, carry considerable zinc and iron and the company had been marketing a zinc concentrate of the composition indicated in the analyses given earlier in this paper. In order to make a marketable zinc concentrate, considerable zinc was lost in an iron-zinc middling product; much of which was taken over into the zinc concentrate when the electrolytic-zinc plant became available. This led to the zinc plant getting a lower grade of concentrate than that with which the preliminary experiments were conducted, which was compensated for, to a certain extent, by an advantageously high iron content in the zinc-plant residues.

The furnace used for roasting is a standard Wedge zinc roaster, 25 ft. (7.6 m.) outside diameter, 21 ft. (6.4 m.) inside diameter, seven roasting hearths with a total hearth area of 2350 sq. ft. (216 sq. m.). Each hearth is rabbled by two arms, carrying ten rabble blades each. The arms on the upper five hearths are air cooled, 5000 cu. ft. (140 cu. m.) of air being blown through them against a pressure of 2.09 oz. per sq. in. by means

TABLE 1.—*Effect of Temperature upon Extraction—Wedge Roaster*

Roaster Feed	Analysis, Per Cent.	Screen Analysis, Per Cent.	
Zn	34.80	plus 40 mesh	27.0
Cu	0.40	40–60 mesh	24.4
Fe	15.50	60–80 mesh	16.2
Mn	0.30	80–100 mesh	7.8
Pb	2.70	–100 mesh	23.1
S	34.80		
Silica	4.70		
Lime	1.15		

Each series covers 24 hr. of uniform operation, and all analyses are based upon composite hourly samples for the entire day.

Series	1	2	3	4	5
Tons feed per 24 hr	27.00	26.0	26.0	26.0	26.0
Tons coal per 24 hr	.....	....	6.0	....	....
Minutes per shaft revolution	4.00	3.0	3.0	3.0	3.0
Approximate hours roast	9.33	7.0	7.0	7.0	7.0
	Hearth Temperature, Degrees C.				
1	405	470	510	450	...
2	650	690	690	730	...
3	660	705	705	750	...
4	590	655	685	690	710
5	600	690	690	735	740
6	600	675	705	745	710
7 Approximately	575	600	600	600	600
Average last six hearths	315	670	672	708	708
Extractions, total zinc per cent., discharged from hearth indicated					
2	3.4	2.5	3.1	4.8	3.5
3	5.1	3.3	23.4	....	19.0
4	9.3	13.0	27.1	19.2	36.6
5	12.9	23.2	30.9	31.5	48.3
6	14.9	41.6	35.0	62.2	57.5
Calcine	17.8	53.2	61.0	79.0	76.9
Water-soluble zinc in calcines, per cent.	2.8	1.6	1.8	1.4	1.1

Comparison Between Series 3 Above and Experimental Roaster

Concentrate Feed	Wedge	Electric
Zinc, per cent	34.80	47.70
Iron, per cent	15.50	4.50
Average temperature, degrees C.	672.00	650.00
Hours roasted	7.00	7.00

Zinc Extractions, Per Cent.	Water Soluble	Total Soluble	Water Soluble	Total Soluble
plus 40 mesh	1.60	43.40	3.97	50.60
40–60 mesh	2.49	51.80	4.22	64.60
60–80 mesh	4.17	60.30	7.17	79.00
80–100 mesh	5.40	70.90	9.45	82.60
–100 mesh	9.80	85.50	13.75	87.50

of a No. 9 Buffalo fan blower. The cooling air is discharged into the space above the sixth and seventh roaster hearths. The arms on the lowest two hearths are water cooled, requiring some 20 gal. (75 l.) of water per minute, which later serves as cooling water for the Baker calcines cooler. The central shaft is driven through a Reeves variable-speed drive and its speed of rotation can be varied between the limits 120 and 270 sec. per rev. Two coal-fired combustion chambers are arranged at diametrically opposite points; their flues conduct the combustion gases into the sixth and seventh hearth chambers. Wilson Mauelein pyrometer couples are arranged in grooves cut into the upper surface of each hearth midway of the active hearth radius; all the couples are connected to multiple recording instrument.

The furnace was started with the intention of keeping temperatures as close to 600° C. as possible. It was soon found that with coarse concentrates and a short roasting period, this temperature was too low for any reasonable roaster tonnage capacity. The temperatures were therefore gradually raised to 700° C. and above with the results shown in Table No. 1. The appended comparison between the roasting rates of

TABLE 2.—*Effect of Changing Speed of Rabble Shaft—Wedge Furnace*

Roaster feed is slightly higher grade than indicated in Table 1 but of about the same screen analysis.

Each series covers twelve consecutive 8-hr. shifts under uniform operating conditions. All data averaged, and analyses refer to composite samples.

	Series 1	2	3
Seconds per shaft revolution	260.00	180.00	150.00
Approximate hours roast	10.00	6.90	5.75
Tons feed per 24 hr.	26.70	32.30	22.00
Tons coal per 24 hr.	6.00	6.60	6.25
	Hearth Temperature, Degrees C.		
1	605	559	518
2	792	790	778
3	742	737	729
4	760	735	725
5	810	770	765
6	772	762	752
7	650	650	650
Average last six hearths	755	727	716
Calcine Analysis			
Total zinc, per cent	44.50	45.50	45.20
Water-soluble zinc, per cent	0.29	0.17	0.30
Total soluble zinc, per cent	38.45	40.05	39.60
Total iron, per cent	12.68	12.08	11.83
Zinc extraction, average 12 shifts, per cent.	86.50	87.90	87.50
Maximum, per cent., best shift	89.7	89.3	89.1
Minimum, per cent., poorest shift	83.0	87.1	84.6
Sulfur dioxide in exit roaster gas, per cent. by volume		1.5–2.0	

TABLE 2 (*Continued*).—*Composite Hearth Samples for all Shifts—Above Series*

Hearth Number	Zinc, Per Cent.			Iron, Per Cent.	Sulfur, Per Cent.		
	Water Soluble	Total Soluble	Extraction		Arsenic Sulfate	Total	Sulfide
			Series 1 (10-hr. roast)				
1	0.00	1.1	2.8	14.0	0.19	23.8	23.6
2	1.35	10.0	23.6	12.7	1.12	17.3	16.2
3	0.20	15.4	35.5		1.09	15.4	14.3
4	0.10	27.9	62.8	12.4	1.43	8.8	7.4
5	0.25	35.5	79.8	12.0	1.35	6.1	4.3
6	0.10	39.3	84.2	11.1	1.74	4.0	2.3
7	0.15	37.3	86.9	12.3	1.78	4.2	2.4
			Series 2 (6.9-hr. roast)				
1	0.05	1.5	3.9	12.5	0.34	24.1	23.8
2	0.15	7.1	17.5	13.0	1.39	17.4	16.0
3	0.20	17.5	40.3	11.4	1.91	12.7	10.8
4	0.20	23.1	56.6	11.8	2.27	8.2	5.9
5	0.65	33.3	75.7	11.4	2.54	6.0	3.5
6	0.30	38.8	87.3	11.9	2.50	4.4	1.9
7	0.05	38.9	86.8	12.0	1.99	4.5	2.5
			Series 3 (5.75-hr. roast)				
1	0.05	1.6	4.1	13.0	0.21	25.6	25.4
2	0.15	8.2	21.8	14.6	1.25	17.5	16.2
3	0.15	15.4	37.7	12.2	1.96	13.9	11.9
4	0.25	22.8	57.8	13.7	2.35	9.7	7.3
5	2.35	33.6	80.3	11.2	3.45	8.2	4.8
6	0.35	36.5	91.0	10.2	2.40	5.5	3.1
7	0.60	39.8	90.5	11.2	2.90	4.9	2.0

the various screen sizes in the Wedge furnace and in the experimental roaster clearly indicates the need for finer grinding of the roaster feed. Finer grinding was impracticable at the time, as the zinc plant was not equipped for grinding concentrates. It was also known that at Trail the use of a very fine roaster feed led to the collection of 7 per cent. dust in the flues and the Cottrell system installed there; the Judge roaster was not equipped for dust collection. The alternative appeared to be to increase the roasting period by slowing down the speed of rotation of the rabble shaft. The results are shown in Table 2.

The extraction and sulfur elimination data given in Table 2 are shown in Fig. 12. Slowing down the rabble shaft slows down the rabbling rate and also leads to a thicker ore bed upon the hearth. Both of these factors lessen the oxidation rate to such a point as to more than offset the effect of the longer roasting period.

The next set of experiments concerned itself with the relations between the rate of feed to the furnace, extraction, and fuel consumption. Here, again, the effect of screen size upon extraction was noted, with the results given in Fig. 13. Comparing these results with those given in Fig. 9 shows that there is a fairly definitely fixed relation between screen size and roasting rate. There is little question but that the concentrates should be reduced to pass at least a 60-mesh screen. The limiting feature is undoubtedly too low an oxidation rate; *i.e.*, it is failure to oxidize sulfur rather than the formation of insoluble ferrites that leads to low extractions in this case. This is brought out by the data relative

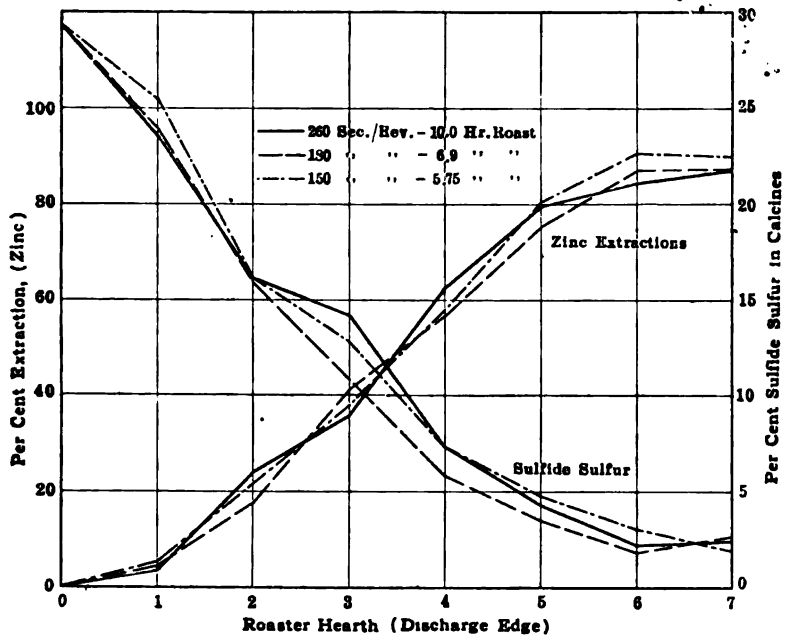

FIG. 12.—JUDGE MINING & SMELTING CO. WEDGE ROASTER. AVERAGE TEMPERATURE, 740° C.; AVERAGE TONS FEED PER 24 HR., 24.

to the nature of the insoluble zinc compounds in the calcines, as given in Table 4.

With the furnace draft and temperature remaining as they were during the above experiments and with the concentrates not further reduced in size, the economic capacity of the furnace does not exceed 28 tons per day with a fuel consumption of about 20 per cent. of the concentrates weight. By grinding to 60 mesh, it is probable that the roaster capacity can be increased to rather better than 35 tons per day with a coal consumption not greatly exceeding 10 per cent. of the concentrates weight. It also appeared possible to increase the oxidation rate by increasing the rabbling rate. The number of blades per rabble arm was

accordingly increased to 15 and the pitch was proportionately decreased. No detailed experiments have been carried out, however, to determine the difference in furnace behavior. For the month preceding the change,

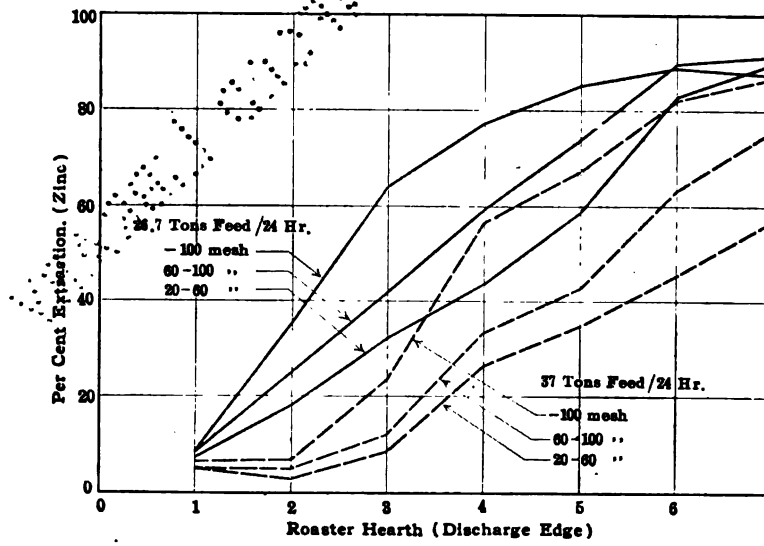

FIG. 13.—JUDGE MINING & SMELTING CO. WEDGE ROASTER. FINENESS VERSUS EXTRACTION. 8.08 HR. ROAST AT 720° C.

TABLE 3.—*Feed Tonnage versus Extraction and Fuel Consumption*

Roaster feed is very nearly the same as in Table 2.
Each series covers 24 hr. operation under uniform conditions.

	Series 1	2	3	4
Tons feed per 24 hr	26.70	30.00	34.00	37.00
Tons coal per 24 hr	5.50	4.75	4.75	4.25
Coal per concentrates, per cent	20.60	15.80	14.00	11.50
Seconds per shaft revolution	210.00	210.00	210.00	210.00
Approximate hours roast	8.08	8.08	8.08	8.08
	Hearth Temperature, °C.			
No. 1	550	524	537	478
No. 2	740	733	756	717
No. 3	720	740	746	756
No. 4	702	716	728	710
No. 5	736	750	756	745
No. 6	702	679	697	699
Average last five above	720	723	737	725
Calcines Analysis				
Total zinc, per cent	43.90	42.70	44.70	45.20
Water-soluble zinc, per cent	0.78	0.68	0.57	0.70
Total soluble zinc, per cent	38.90	34.80	35.70	34.70
Total iron, per cent	9.50	7.70	7.10	8.60
Extraction, zinc, per cent	88.60	81.50	78.90	76.80

Screen Sizes versus Extraction (Best Shift Sample Above Series)

	Series 1			Series 4		
Tons feed per 24 hr.....	26.7			37.0		
Screen sizes.....	20–60	60–100	–100	20–60	60–100	–100
Extractions, zinc, per cent.						
Hearth No. 1.....	7.8	8.0	7.5	5.0	5.4	7.0
Hearth No. 2.....	18.2	25.8	35.3	3.3	4.7	7.0
Hearth No. 3.....	32.3	41.7	64.0	8.2	13.6	23.9
Hearth No. 4.....	43.8	59.2	76.8	26.9	33.8	56.5
Hearth No. 5.....	58.2	73.9	85.2	34.3	42.5	67.2
Hearth No. 6.....	82.8	89.5	88.7	45.3	63.6	82.0
Calcine.....	90.0	91.8	87.6	56.6	75.7	86.4
Whole sample.....		91.6			78.2	
Average total zinc, per cent.	50.3	48.4	49.9	39.6	42.7	45.9
Average total iron, per cent.	6.6	8.0	8.8	17.2	11.7	11.8

TABLE 4.—*Disposition of Insoluble Zinc in Judge Calcines*

Table 2 Series	1	2	3
Tons feed per 24 hr.....	26.70	23.30	22.00
Roaster temperature, degrees C.....	755.00	727.00	716.00
Hours roasted.....	10.00	6.90	6.25
Total iron in calcine, per cent.....	12.68	12.08	11.83
Total zinc in calcine, per cent.....	44.50	45.50	45.20
Total soluble zinc, per cent.....	38.45	40.05	39.60
Insoluble zinc, per cent.....	6.05	5.45	5.60
Sulfide sulfur, per cent.....	2.40	2.50	2.00
Assuming all sulfide sulfur combined as ZnS			
Zinc as ZnS, per cent.....	4.91	5.12	4.09
Total insoluble zinc, per cent.....	6.05	5.45	5.60
Zinc as ferrites, by difference, per cent.....	1.14	0.33	1.51

Table 3 Series	1	2	3	4
Tons feed per 24 hr.....	26.70	30.00	34.00	37.00
Roaster temperature, degrees C.....	720.00	727.00	739.00	725.00
Hours roasted.....	8.08	8.08	8.08	8.08
Total iron in calcine, per cent.....	9.50	7.70	7.10	8.60
Total zinc in calcine, per cent.....	43.90	42.70	44.70	45.20
Total soluble zinc, per cent.....	38.90	34.80	35.70	34.70
Insoluble zinc, per cent.....	6.00	7.90	9.00	10.50
Sulfide sulfur, per cent.....	2.00	3.50	4.03	5.02
Zinc as ZnS, per cent.....	4.09	7.15	8.25	10.30
Total insoluble zinc, per cent.....	6.00	7.90	9.00	10.50
Zinc as ferrite, by difference, per cent.....	1.91	0.75	0.75	0.20

the average tonnage roasted per day was 28, with calcines yielding 90 per cent. zinc extractions. For the month following the change, and with no other alterations in feed or practice generally, the calcines averaged a trifle over 92 per cent. soluble zinc. It appears that at 28 tons feed rate the extraction was improved by about 2 per cent., and that for the same extraction the capacity of the furnace was raised to about 32 tons per day.

A greater rabbling frequency would seem better practice in a new furnace installation, but it would be better to add arms than to add more rabble per arm, as fifteen rabbles per arm brings the blades rather too close together. Reversed blades may be used on one arm on each hearth, as in the small electric roaster, so that the ore bed may be stirred without translating it across the hearth so rapidly.

Greater capacity might be obtained by increasing the roaster temperature, but a material increase in temperature above 750° C. greatly increases maintenance costs and service interruptions.

Discussion of Roasting Data

Roasting in General.—Roasting is essentially a diffusion process. Mobile, gaseous oxygen must be brought into contact with relatively immobile, solid, sulfide molecules in order to effect oxidation of the latter. A cube of blende that will pass a 100-mesh screen contains some 10^{16} molecules of zinc sulfide of which less than one millionth are freely exposed to oxidation at the surface of the cube. In order to contact with and oxidize the interior molecules that make up the mass of the ore particle, oxygen must diffuse into the ore particle. It would appear that this alone might fix the relative roasting rates of variously sized ore particles in that given roasting conditions would lead to the oxidation of a surface layer of uniform thickness.

Roasting of Judge Concentrates at 650° C.

	Mesh 40–60	60–80	80–100
Maximum screen opening, mm	0.317	0.211	0.157
Minimum screen opening, mm	0.211	0.157	0.127
Average side equivalent cube	0.264	0.184	0.142
Average volume of cube, mm³	0.01834	0.00623	0.00286
Hours Roasted	Extraction, Per Cent. Zinc		
5.5	35.1	43.1	52.5
7.0	64.6	79.0	82.6
9.0	90.0	92.0	93.0
	Thickness of Oxidized Surface Layer, in Millimeters, as Calculated from Extractions		
5.5	0.018	0.015	0.015
7.0	0.039	0.038	0.031
9.0	0.142	0.105	0.084

The agreement here is too good to be wholly accidental. The diffusion rate of oxygen into the ore particle, and thus the roasting rate, must be determined by the oxygen concentration at the surface of the individual ore particle. Oxygen must diffuse into the ore bed before it can diffuse into the ore particle itself, and the relative rates of oxidation on the hearth and during the dropping of the ore particles from hearth to hearth through the roaster gas and the relative rates of oxidation in the ordinary roaster, as compared with the Dwight Lloyd machine or the "porous hearth" blast roaster described by Greenawalt,[2] would indicate that the first diffusion step is as great a limiting feature as is the second.

Diffusion into the ore bed can be, in part, set aside by mechanical means, that is, by rapid and frequent stirring or rabbling, or by forcing the roaster gas through the ore bed. For example, it is reported that considerable success has been attained in Australia recently in blast roasting zinc-sulfide ores for the retort smelter. Diffusion into the ore particle itself is beyond control except so far as it can be accelerated by increasing temperatures. It will reach its maximum rate when the oxygen concentration at the surface of the ore particle is the same as the oxygen concentration in the roaster gas as a whole. This is very important in its bearing upon fuel consumption in roasting. The energy of combustion of the average zinc concentrate is sufficient to heat to the roaster temperature some three times the amount of air required for its oxidation yet the cost of the fuel used for roasting zinc concentrates is by far the greater item in the cost of roasting. This will be taken up later in discussing the energy balance determined for the Wedge roaster at the Judge plant.

Roasting of Zinc Sulfide to Oxide and Sulfate.—Zinc sulfate can be formed through any one of the following reactions:

$$ZnS + 4O = ZnSO_4$$
$$ZnS + 3O = ZnO + SO_2$$
$$ZnO + SO_2 + O = ZnSO_4 \qquad (a)$$
$$ZnO + SO_2 + Fe_2O_3 = ZnSO_4 + 2FeO \qquad (b)$$
$$2FeO + O = Fe_2O_3$$
$$ZnO + SO_3 = ZnSO_4 \qquad (c)$$

There is considerable evidence that the first reaction is responsible for most of the sulfate formed. The only gaseous reagent is oxygen and there are no gaseous reaction products, therefore, the oxygen concentration alone should mainly determine the amount of sulfate formed. Reactions (*a*) and (*b*) involve two gaseous reagents, so that the amount of sulfate formed will be determined mainly by the product of the concentrations of oxygen and sulfur dioxide.

[2] "Hydrometallurgy of Copper." 130. N. Y., 1912. McGraw-Hill Book Co.

In the case of Bully Hill ore, see Fig. 2, no appreciable amount of sulfate was formed until the sulfur-dioxide concentration fell below 2 per cent. Beyond this point, when the sulfur-dioxide concentration averaged much below 1 per cent., 73 per cent. of the zinc was oxidized and 94.5 per cent. of that was oxidized to sulfate. Of the added sulfur oxidized during this later stage, more than 50 per cent. was converted to sulfate. It was found that increasing the air rate, which raises the oxygen concentration in the roaster gas and lowers the sulfur-dioxide concentration, rapidly increased the amount of sulfate formed.

In roasting the high-grade Butte Superior concentrates, see Fig. 5, no appreciable amount of sulfate was formed until the sulfur-dioxide concentration fell below 2 per cent. During the first 4 hr. of the roasting period, when the sulfur-dioxide concentration exceeded 2 per cent., 82 per cent. of the zinc was oxidized. During the later period, and while the sulfur-dioxide concentration averaged so low that one could breathe the roaster gas without serious discomfort, an added 17 per cent. of the zinc was oxidized and 85 per cent. of this was converted to sulfate. Finely ground ore should lead to higher oxygen concentrations at the contact between the interior zinc-sulfide molecules and the roaster gas, since it should lead to thinner diffusion diaphragms; it is to be noted that fine ore particles consistently lead to greater amounts of zinc sulfate.

It is by no means clear why a high iron content should lead to the formation of more sulfate than a low iron content, but when the low iron content Butte Superior concentrate was roasted in the same manner as the high iron Bully Hill ore, the Butte Superior concentrate yielded only 20 per cent. of its zinc as sulfate while the Bully Hill ore yielded 76 per cent. This relation appears to carry through all of the experimental work done; a high iron content seems essential to the formation of large amounts of zinc sulfate in spite of the fact that, during that part of the roasting period when the zinc sulfate is formed, nearly the same proportion of the remaining zinc sulfide is converted to sulfate.

Zinc sulfate decomposes when it is heated above 575° C., the rate of its decomposition increasing rapidly as the temperature is increased. This is clearly shown in Fig. 4 and agrees with the known chemistry of zinc sulfate. Woehler and Plueddemann[3] studied the decomposition pressures of zinc sulfate heated to various temperatures in closed vessels and Mostowitsch[4] studied the decomposition of zinc sulfate heated to various temperatures in dry air currents. Mostowitsch showed that zinc sulfate heated in the presence of iron oxide decomposed more rapidly than zinc sulfate heated alone, which indicates a definitely exothermic reaction between zinc oxide (or sulfate) and iron oxide to form ferrites. He further showed that the presence of silica did not

[3] *Berichte Deut. Chem. Ges.* (1908) **41**, (1), 703. [4] *Metallurgie* (1911) **8**, 763.

accelerate the decomposition rate of zinc sulfate until the temperature exceeded 1000° C., indicating that zinc silicate is not formed below that temperature. The data of Woehler and Plueddemann and of Mostowitsch have been plotted in Fig. 14.

Mostowitsch further showed that the breaking up of zinc sulfate at 750° C. required 24 hr. for its completion. It is not, then, a rapid reaction at such temperatures we are concerned with. His data, plotted in Fig. 15, are consistent with the existence of one, and only one, reaction product intermediate between zinc sulfate and zinc oxide, and the

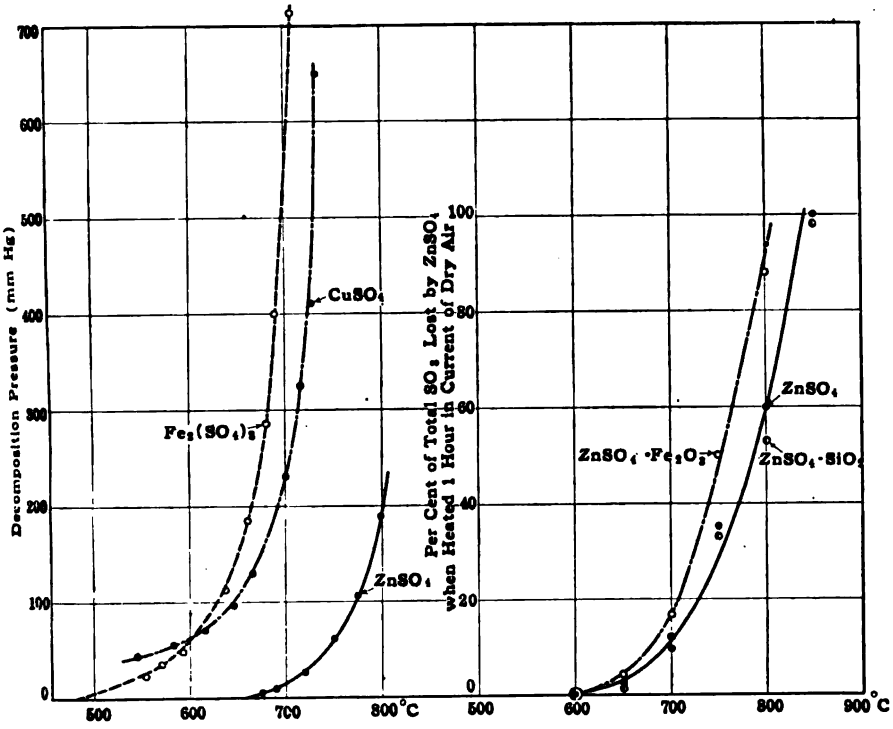

FIG. 14.—DECOMPOSITION PRESSURE OF METAL SULFATES HEATED IN CLOSED VESSELS. (*Data by Wöhler and Plüddemann and by Mostowitsch. See footnotes.*)

break in the curve indicates this to be a basic zinc sulfate of the composition $ZnO:2ZnSO_4$. This same compound, in hydrated form, is found in the zinc leaching plant, where it is distinctly disadvantageous. It is formed by the direct solution of zinc oxide in neutral zinc-sulfate solution; it is formed through the precipitation of zinc hydrate when lime is added to coagulate the leaching solutions and by the action of metallic zinc upon zinc-sulfate solution with the liberation of hydrogen during the purification processes. That basic sulfate is to be found in roasted calcines is at times indicated by the presence of sulfur, which is insoluble in water but readily soluble in dilute hydrochloric acid. The highest val-

ues found for such basic sulfate sulfur were determined in Bully Hill calcines, which contained 0.74 to 0.89 per cent.

Formation of Zinc Ferrites.—The writer uses the term "ferrites" from mere habit. Hamilton, Murray, and McIntosh[5] use the more chemically correct term "ferrates" in describing work they did at Trail in the way of synthetizing ferrates by heating together intimately mixed portions of pure zinc and iron oxides. By heating molecular proportions of

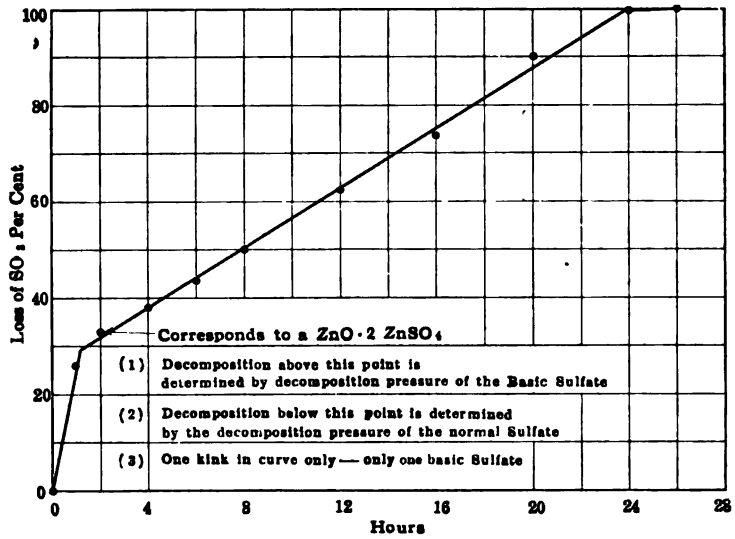

FIG. 15.—DECOMPOSITION OF ZINC SULFATE HEATED AT 750° C. IN DRY AIR CURRENT (*Data by Mostowitsch.*)

zinc oxide and ferric oxide at various temperatures, they found that the zinc oxides became insoluble. The following data are interpolated from their plots:

TEMPERATURE, DEGREES C.	ZINC RENDERED INSOLUBLE IN 5 HR., PER CENT.
593	0
648	73
704	82
759	91
815	100

From similar experiments, in which the proportions of zinc oxide and ferric oxide were varied, they concluded that no ferrates were formed that contain more zinc than $ZnO \cdot Fe_2O_3$, but that when these oxides are heated for any length of time above 650° the iron will render one-half its equivalent of zinc insoluble. They also give the results obtained in heating thirteen various ores in a small hand-rabbled muffle furnace at

[5] *Min. & Sci. Pr.* (Aug. 11, 1917) **115**, 195.

750–800° C. They found that the majority of the ores yielded calcines in which the insoluble zinc and total iron bore simple molecular ratios, but that some of the calcines, notably those from the Sullivan ores, carried much less insoluble zinc than was to be expected from their iron content. Their explanation is of decided interest.

"In some way, therefore, the combination is prevented from being as complete as one should expect from the composition of the ore. One explanation may be that at this concentration of the zinc and iron another compound may be formed than that represented by the formula $ZnO \cdot Fe_2O_3$, but we have been unable to prove this and regard the existence of any combination except $ZnO \cdot Fe_2O_3$ aq unlikely. On the other hand, it may be that free crystals of pyrrhotite do not combine as readily with those crystals which are directly attached to crystals of blende, or as that iron which may be isomorphous with the zinc in the blende."

The experimental data presented here were selected to cover the various ore types mentioned, and it seems that the experimental results leave little doubt as to the correctness of the above explanations.

The Daly Judge ores contain pure blende and pure pyrite, so coarsely crystallized that the crystals can be separated and analyzed to make sure that the zinc and iron are not isomorphous. Furthermore, the minerals are so coarsely crystallized that the major fraction of the particles of concentrate roasted are either blende or pyrite and seldom part one and part the other. The concentrates were coarse which made it necessary to roast them for long periods at temperatures well above the known formation temperature of the ferrates. In spite of this, the resulting calcines contained but from 3.2 to 14.1 per cent. of the insoluble zinc called for by the iron content and the ferrate formula.

Bully Hill ore is a massive sulfide in which the minerals are so finely divided and intermixed that it is practically impossible to identify blende or pyrite. But the ore contains sufficient sulfur to account for the iron as pyrite and sulfur is volatilized in roasting. This is presumptive evidence against isomorphous crystallization since the isomorphously crystallized iron is invariably FeS rather than FeS_2. The ore, however, is so finely crystallized that the average roaster feed particle must contain both blende and pyrite attached to one another. The careful roasting of Bully Hill ore below the formation temperature of ferrates led to 93.6 per cent. zinc extractions, leaving insoluble zinc in the calcines amounting to but 15.7 per cent. of that called for by the iron content and ferrate formula. Roasting for long periods at 700° C. led to 65 per cent. extractions and to calcines containing 86 per cent. of the insoluble zinc called for by the iron and ferrate formula. It is probable that the calcines contained some sulfide sulfur, which would still further reduce the amount of insoluble zinc accounted for as ferrates in the above.

Broken Hill concentrates appear to consist of isomorphously crystal-

lized zinc and iron sulfides. No pyrite is obtrusively visible and the concentrates do not contain sufficient sulfur to account for the iron as anything but FeS. No manner of roasting, either below or above the formation temperature of ferrate, led to extractions higher than 87–88 per cent., and the same extraction was invariably obtained so long as the sulfides were oxidized. The amount of insoluble zinc left in the calcines is slightly greater than that called for by the iron content.

The Frisco concentrates appear to be made up of isomorphously crystallized iron and zinc sulfides, and the highest extraction obtained still left in the calcines 80 per cent. of the insoluble zinc called for by the ferrate formula.

The formation of ferrates can take place in but two ways: The reaction takes place between two solid oxides or one (or both) of the oxides must be sufficiently volatile to distil into contact with the other. It seems more probable that the first is the more important and that unless the iron and zinc are isomorphously crystallized there must be mutual diffusion of one oxide into the other before the reaction can take place. Diffusion is, at best, an extremely slow process, hence ferrates are formed readily only when the zinc and iron are isomorphous. When blende and pyrite are firmly attached to one another there is, at least, a common contact plane through which diffusion can take place. Probably no ferrate is formed if the temperature is kept sufficiently low, and more ferrate is formed as the temperature is raised and the diffusion rate is increased. Ores of this type, like the Bully Hill ore, can be commercially roasted to yield far better extractions than ores containing similar amounts of zinc and iron that are isomorphous.

Finally, when the roaster feed is made up mainly of separate particles of blende and pyrite, as in the case of the Judge concentrates, and possibly in the case of the Butte Superior concentrates, there are only casual contacts between the iron and zinc particles through which diffusion can take place and the formation rate of ferrate is so low that it scarcely enters into the roasting problem at all.

Solubility of Iron in Roasted Calcines.—Much dire distress was predicted in connection with the leaching of ferruginous calcines. Iron is very readily oxidized and the trouble in the leaching plant has been due to leaching too little iron rather than too much. At Bully Hill, the average leaching solution, made up to 100 gm. zinc per liter by leaching calcines with acid and water, contained 0.020 gm. of iron per liter. Later on, when it was found that dissolved iron was essential to the complete removal of arsenic and antimony, we tried to so roast the ore that more iron would dissolve; to use such acid concentrations as would lead to dissolving more iron; and finally purchased iron and iron salts as being the cheaper alternative. The solubility of iron at various stages of the

roasting process is indicated by the following data taken from the Wedge furnace at the Judge plant (experimental series 1, Table 2):

Hearth Number	Soluble Iron Based on Calcines, Weight Per Cent.
1	0.3700
2	0.2870
3	0.2255
4	0.1292
5	0.0431
6	0.0046
7	0.0015

Behavior of Manganese.—Practically all the manganese dissolved in the leaching plant is present in the calcines as manganese sulfate, which is stable at higher temperatures than zinc sulfate. Ordinarily, about 10 per cent. of the manganese present in the calcines will be dissolved in the leaching plant.

Behavior of Silica.—A bugaboo in the shape of "colloidal silica" has traveled about the various electrolytic-zinc plants and great importance has been attached to tracing it to its source. The natural oxidized zinc ores (oxide, carbonate, and hydrated silicate) frequently do give trouble in the leaching plant since considerable amounts of silica can be dissolved from them and it requires but 2 or 3 gm. of silica to gel a liter of solution. All siliceous calcines worked with have yielded very small amounts of silica to the solution and it does not appear that the amount of silica dissolved bears any relation to the source of the roaster feed, nor to its total silica content. Trouble from dissolved silica has frequently been traced directly to the lime or limerock used for neutralizing and coagulating the leach solution; probably this is the more frequent source of trouble.

Behavior of Bases.—The acid consumption in leaching various calcines makes it appear that both lime and magnesia are converted to sulfate in the roaster. In no case has it appeared that these bases consumed acid in the leaching plant. Magnesium sulfate is a cumulative impurity in the zinc-plant solutions but it has not been of any importance in any instance as yet on record.

Behavior of Lead.—Lead sulfide is converted to lead sulfate during the early stages of the roast and is left in the calcines as sulfate, since the lead can be almost completely extracted from either the calcines or from the leach-plant residues with strong sodium-chloride solution. It does not appear that any insoluble lead-zinc compounds are formed but there is a very marked tendency for high lead concentrates to sinter in the early stages of the roasting process.

Behavior of Arsenic and Antimony.—Both arsenic and antimony are volatilized in roasting, but not so completely as to render them unimportant in the calcines. In roasting ores from the North Star mine (Hailey, Ida.) in the small electric roaster, the outlet air tube became choked with

arsenic trioxide shortly after the roasting had started, and further evolution of arsenic soon ceased.

Hours at 650° C.	Arsenic in Calcines, Per Cent.
0	2.96
5	0.25
10	0.20
20	0.20

Antimony appears to be less completely volatilized than arsenic. From the operating standpoint, it matters little whether the roaster feed carries a fair fraction of arsenic and antimony, or whether it carries a barely detectable trace of them. In either case enough arsenic and antimony will be dissolved to cause need for their removal from the leaching solution.

Behavior of Copper.—Ordinarily the roasting temperature used in roasting for zinc extraction is too high to yield a high copper extraction. As much as 50 per cent. of the total copper has been dissolved in regular practice, but the average is probably nearer 20 per cent.

Acknowledgments

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Appendix

Heat Balance-Judge M. & S. Co. Wedge Roaster

Combustion Heats		Kg. Calories		
		Per Mol.	Per Kg. of Metal	
Calcine				
$ZnS + 4O$	$= ZnSO_4$	186.6	2850	Zinc
$ZnS + 3O$	$= ZnO + SO_2$	111.1	1700	Zinc
$PbS + 4O$	$= PbSO_4$	195.4	945	Lead
$2FeS_2 + 11O$	$= Fe_2O_3 + 4SO_2$	425.2	3800	Iron
$As_2S_3 + 9O$	$= As_2O_3 + 3SO_2$	334.0	2230	Arsenic
$Sb_2S_3 + 9O$	$= Sb_2O_3 + 3SO_2$	340.4	1420	Antimony
$CuS + 3O$	$= CuO + SO_2$	98.9	1555	Copper

Coal, Rock Springs, Wyo.[a]

	Per Cent.	
H	5.36	
O	21.04	
C	66.15	
Ash	5.48	
B.t.u. per pound	11,800	6550 Kg. cals. per kg.

Net oxygen required for complete combustion, 1.984 kg. oxygen per kg. coal.

[a] Analyses and combustion data from Marks' Handbook; analysis as received (8.53 per cent. moisture).

Roaster Data Series	1	2	3	4
Tons concentrate per day	26.70	30.00	34.00	37.00
Tons coal per day	5.50	4.75	4.75	4.25
Concentrates analysis				
Zinc (as ZnS), per cent	39.90	38.90	40.60	41.20
Iron (as FeS_2), per cent	8.63	7.00	6.46	7.82
Lead (as PbS) average, per cent	3.00	3.00	3.00	3.00
Arsenic (as As_2S_3) average, per cent	0.30	0.30	0.30	0.30
Antimony (as Sb_2S_3) average, per cent	0.30	0.30	0.30	0.30
Copper (as CuS) average, per cent	1.00	1.00	1.00	1.00
Disposition of above constituents in final calcines				
Zinc to sulfate, per cent	1.78	1.59	1.28	1.55
Zinc to oxide, per cent	89.00	81.70	80.30	75.65
Zinc as sulfide, per cent	9.22	16.71	18.42	22.80
Assumed				
Lead to sulfate, per cent	100.00	100.00	100.00	100.00
Iron to Fe_2O_3, per cent	100.00	100.00	100.00	100.00
Copper to CuO, per cent	100.00	100.00	100.00	100.00
Arsenic-antimony to M_2O_3, per cent	100.00	100.00	100.00	100.00

Heat Supplied

Per ton concentrates charged to roaster kg. calories.

	1	2	3	4
ZnS to oxide	545,000	493,000	502,000	481,000
ZnS to sulfate	18,300	16,000	13,400	16,400
PbS to sulfate	25,700	25,700	25,700	25,700
Fe_2S_3 to Fe_2O_3	297,000	241,000	222,000	269,000
As_2S_3 to As_2O_3	6,000	6,000	6,000	6,000
Sb_2S_3 to Sb_2O_3	4,000	4,000	4,000	4,000
CuS to CuO	14,000	14,000	14,000	14,000
Total concentrate	910,000	799,700	787,100	816,100
Coal per ton concentrates	1,300,000	996,000	873,000	725,000
Total per ton concentrates	2,210,000	1,795,700	1,660,100	1,541,100
Total heat supplied to roaster per day, kg. calories				
Tons concentrate	26.7	30.0	34.0	37.0
Total kg. calories $\times 10^6$	59.0	53.9	56.4	57.1
Distribution of heat supplied				
Per cent. supplied by concentrate	41.2	44.5	47.3	52.8
Per cent. supplied by coal	58.8	55.5	52.7	47.2
	100.0	100.0	100.0	100.0

HEAT ACCOUNTED FOR, KG. CALORIES × 10^6 PER DAY

Series	1	2	3	4
CALCINES:				
Tons calcine	24.20	27.00	30.60	33.30
Temperature, degrees C., approximate	700.00	700.00	700.00	700.00
Calories × 10^6 per day	2.94	3.28	3.71	4.04
COOLING WATER:				
25 gal. per min.				
Incoming temperature, 8° C.				
Outgoing temperature, 37° C.				
Calories × 10^6 per day	2.99	2.99	2.99	2.99
RADIATION:				
Total exposed surface	3000 sq. ft.			
Mean effective temperature	65° C.			
Radiation-watts per sq. ft	42, approximate			
Calories × 10^6 per day	2.70	2.70	2.70	2.70
MOISTURE IN CONCENTRATE, EVAPORATED ON DRIER HEARTH:				
Per cent. moisture average	3.00	3.00	3.00	3.00
Tons moisture per day	0.77	0.90	1.02	1.11
Calories × 10^6 per day	0.42	0.49	0.55	0.60
MOISTURE IN COAL, ELIMINATED AT STACK TEMPERATURE:				
Per cent. moisture, approximate	5.48	5.48	5.48	5.48
Tons moisture per day	0.30	0.26	0.26	0.23
Calories × 10^6 per day	0.23	0.19	0.19	0.17
STACK LOSSES, TOTAL SUPPLIED LESS THAT ACCOUNTED FOR ABOVE:				
Calories × 10^6 per day	49.82	44.25	46.26	46.60
DISTRIBUTION OF HEAT ACCOUNTED FOR, IN PER CENT. OF TOTAL:				
In calcine	4.98	6.09	6.58	7.06
In cooling water	5.07	5.55	5.31	5.24
By radiation	4.58	5.02	4.80	4.73
By moisture in concentrates	0.71	0.91	0.98	1.05
By moisture in coal	0.39	0.35	0.34	0.30
In stack gases	84.30	82.10	82.00	81.60
Total	100.00	100.00	100.00	100.00

Gas Volumes, Gas Temperatures, Stack Heat Losses.—As previously stated, the pyrometer couples in this roaster were installed in grooves

cut into the upper surface of each hearth. The temperatures reported throughout are calcine temperatures rather than gas temperatures. The following comparison of gas and calcine temperatures covers one day's operation under uniform conditions: the usual pyrometer installation is made with the thermocouples so arranged as to measure gas temperatures rather than calcine temperatures. It is the calcine temperature which determines ferrite formation, and not gas temperature directly. We had trouble with the couples placed in the hearth in that as the hearth raised the couples were pried out and caught by the rabble blades.

Hearth Number	Temperatures, Degrees C.	
	Hearth	Gas
1	495	400
2	690	590
3	660	585
4	700	575
5	735	600
6	730	685
7	700	450

This is the only direct comparison at present available and in that which follows it is assumed that the difference between calcine temperature and gas temperature remains as above.

Series	1	2	3	4
Temperature first hearth	550	524	537	478
Temperature stack gas, approximate	455	429	442	383
Calories $\times 10^6$ (accounted for by difference) in stack gases, as per heat balance	49.8	44.3	46.3	46 6
Corresponding gas volumes, referred to 10° C. and 7500 ft. altitude:				
Cubic meters per day $\times 10^3$	477	462	468	546
Cubic feet per minute	11,700	11,300	11,450	13,350
Sulfur dioxide, volume percentage calculated from sulfur burned and above gas volumes:			1.77	1.63
Calculated per cent. SO_2	1.45	1.59		
Determined per cent. SO_2			2.0	
Air volume required to theoretically account for complete combustion of coal and concentrates as above, assuming 100 per cent. utilization of oxygen contained in air, cubic feet air per minute:				
By concentrates	1,315	1,245	1,400	1,500
By coal	1,170	1,045	1,060	910
Total	2,485	2,290	2,460	2,410
Corresponding maximum SO_2 content obtainable, with coal consumption as given:				
Per cent. SO_2	7.50	8.02	8.42	8.95

The agreement between the calculated sulfur-dioxide concentrations in the roaster gas and the determined concentrations is sufficiently close to fix the air-feed volume between 10,200 and 11,450 cu. ft. (285 and 320 cu. m.) per min. for series 3. It is to be noted that the mean of these volumes [10,825 cu. ft. (303 cu. m.) per min.] is something like 7.8 times the air volume theoretically required for the oxidation of the concentrates, and something like 4.4 times as great as the air volume theoretically required for the concentrates and for the coal actually consumed.

More than 80 per cent. of the heat supplied to the roaster is accounted for in the stack gases, and it would appear that a very considerable reduction in coal consumption could be brought about by reducing the amount of air fed to the roaster without materially affecting the operation of the furnace. With the furnace arranged as at present any additional air fed to the furnace must be heated to the stack temperature (at least) through combustion of coal and at the expense of oxygen contained in that air. It does not appear at all impossible that the use of an excessive volume of air might actually lead to lower oxygen concentrations in the roaster gas, and thus to lower oxidation rates and to lower roaster capacities.

The following calculations, based on the roasting of 30 tons of concentrates per day, as in series 2, are at least interesting in that they indicate some possibilities of air volume control.

ALL AIR VOLUMES REFERRED TO 10° C. AND 7500 FT. ALTITUDE

(Judge Plant)

Cubic feet air per minute	2,290	4,000	6,000	8,000	10,000	12,000	20,000
Cubic feet per minute to stack	1,920	3,640	5,640	7,640	9,640	11,640	19,640
Kg. cals. $\times 10^6$ accounted for per day in stack gases leaving at 450° C	9.5	15.1	23.3	31.5	39.7	48.0	81.0
Kg. cals. $\times 10^6$ accounted for per day in calcines, cooling water, radiation, etc., see heat balance	9.7	9.7	9.7	9.7	9.7	9.7	9.7
Total kg. cals. $\times 10^6$	19.2	24.8	33.0	41.2	49.4	57.7	90.7
Kg. cals. $\times 10^6$ supplied by concentrates in roasting them	24.0	24.0	24.0	24.0	24.0	24.0	24.0
Kg. cals. $\times 10^6$ required from coal to balance	−4.8	0.8	9.0	17.2	25.4	33.7	65.7
Coal required to supply needed heat assuming 100 per cent. combustion efficiency:							
Kg. per day	0.0	115	1,290	2,470	3,640	4,830	9,450
Per cent. of concentrates weight	0.0	0.4	4.9	9.1	13.9	18.5	36.1
Per cent SO_2 in roaster gas	8.0	4.3	2.7	2.0	1.6	1.3	0.8
Per cent. oxygen in roaster gas (*a*) assuming no coal consumed, (*b*) with coal consumption as indicated:							
Per cent. O, (*a*)	10.4	13.8	15.8	16.9	17.5	17.9	18.7
Per cent. O, (*b*)	10.4	13.6	14.6	15.3	15.7	15.9	16.4

If we assume that the oxidation rate, and therefore the roaster capacity, is proportional to the oxygen concentration, and this is an ultra-conservative assumption in this case, the relation between air

volume, roaster capacity, and fuel consumption must be something like the following:

Cubic Feet of Air per Minute	Relative Per Cent., Roaster Capacity	Per Cent., Fuel Consumption	Tons Coal per Ton Concentrate
4,000	86.5	2.9	0.004
6,000	93.0	35.3	0.049
8,000	97.5	65.5	0.091
10,000 (assumed unit)	100.0	100.0	0.139
12,000	101.3	133.3	0.185
20,000	104.5	253.0	0.361

It appears quite certain that there is more to be gained in fuel economy through careful study of air volumes than there is to be gained in greater roaster capacity through the use of excessive air volumes.

The Wedge type of furnace was probably developed to serve the particular purpose for which it is mainly used, that is for the incomplete combustion of sulfides without need for outside fuel, rather than for such complete combustion as is necessary in roasting zinc concentrates. There is little or no indication that this type of furnace cannot be well adapted for the roasting of zinc sulfides, as well adapted perhaps as any other type of furnace, but it is possible that it will require considerable study and, possibly, some special development of the furnace and practice, before completely satisfacrory and most economical operating conditions are both realized.

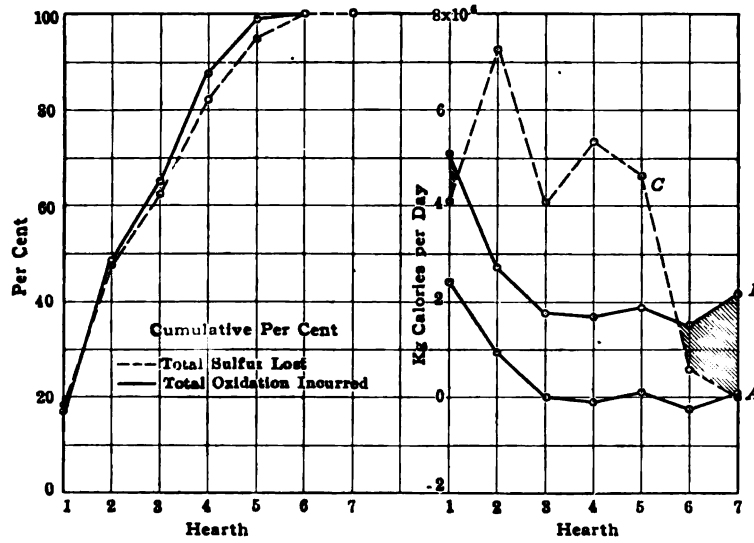

Fig. 16.

The furnace is at present updrafted, and the calcines pass downward through the furnace. The major fraction of the heat evolved by the burning sulfide is liberated in the upper parts of the furnnce, is imparted

to the roaster gas, and is carried on upward through the furnace. In the lower parts of the furnace, insufficient heat is evolved to maintain the temperature required for complete combustion in reasonable time. This is brought out in Fig. 16, where curve *A* indicates the amount of heat absorbed by the calcines (weight, specific heat, and temperature of the calcines); curve *B* indicates the total amount of heat accounted for on each hearth in cooling water, by radiation, and absorbed by the calcines; curve *C* indicates the amount of heat evolved on each hearth by the combustion of the sulfides. The shaded area between curves *B* and *C* represents an amount of heat that must be supplied merely to maintain the roaster temperature, and the unshaded area between the same two curves represents heat that should be available for supplying the deficiency on the lower hearths and for heating the roaster gases, without resort to the use of coal or other fuel.

It is clear that so long as the furnace is updrafted there is no possibility of utilizing the excess heat in the upper parts of the furnace to make up the deficiencies in the lower parts of the furnace. That deficiency, which must be made up through the use of other fuel, amounts to 3,000,000 kg.-cal. per furnace per day and is made up almost wholly of cooling water losses and radiation, both of which can be reduced somewhat. In addition (at the Judge plant, and it is the usual arrangement), some 5000 cu. ft. per min. of air, used in cooling the upper rabble arms and thus heated to 165° C., is discharged into the fifth hearth chamber and must be heated to about 600° C. if it is not to cool that hearth materially. The heat required to heat this air is supplied by the combustion gases from the coal-fired grates; and in order to effect the 600° C. average temperature in the hearth chamber these combustion gases are actually maintained at nearly 1400–1500° C. (as measured in the flues that connect the coal-fired combustion chambers with the roaster). Less than 5 per cent. of the oxygen required for the combustion of the sulfides is consumed on the lowest three hearths, and evidently only a very few hundred cubic feet of air per minute would be sufficient for this purpose. The excessive amount of air introduced into the fifth hearth chamber, however, makes it necessary either to add very much larger quantities of hot combustion gases in order to heat this air, or else to add smaller quantities of combustion gas heated to excessive temperatures. Under the conditions maintained while the experiments were in progress, the temperatures in the combustion gas flues were such that only silica brick would stand up, and it is evident that one cannot get much further on by heating still smaller combustion gas quantities to still higher temperatures. It would seem that better results could possibly be obtained by either discharging a fair part of the air used for cooling the rabble arms outside the furnace or, at least, higher up in the furnace.

Again, the major item of upkeep expense of the roaster has certainly been occasioned by the extremely hot gases entering the roaster from the firebox flues. It would not appear at all impossible that much of this trouble could be done away with, and that the roaster could be made virtually independent of outside fuel, by downdrafting all the furnace, or at least the lower five hearths. To do this would probably require exhaust fans, since otherwise noxious gases would probably fill the roaster building whenever a roaster door was opened; but this does not seem to be a very decided disadvantage. Neither does it appear impossible to substitute electrical energy for fuel firing, with the furnace otherwise unaltered as regards the draft arrangement. At most, it would require the supply of some 3,000,000 kg.-cal. to the roaster per day at a temperature potential well within the reach of metal heaters. This amounts to a continuous load of some 145 kw. per furnace, and this could certainly be reduced if a little attention were paid to the rabble arms and furnace walls of the lowest hearth chamber. An electrolytic-zinc plant must in any case have cheap power, say 0.4 to 0.5 c. per kw.-hr. Good coal scarcely exists in the districts where electrolytic-zinc plants appear to have their most promising future, and even poor coal in some of these districts is very expensive. The writer has in mind one prospective plant for making 150 tons of spelter per day where coal yielding 8000 B.t.u. per lb. will cost $12 to $15 per ton, and where power will not exceed $15 per hp.-yr. The use of power, say at the rate of 100 to 200 kw. per furnace, with a furnace capacity of 30 to 40 tons per day is by no means out of question as regards the relative costs of power and coal, and it would appear possible that the use of power would lead to a more uniform roaster practice.

Again, the writer has in mind several interruptions of service at the Judge plant during recent winters through failure of the coal supply and through failure of the transport service between the coal mine and the zinc plant coal bunkers. The question of fuel economy and of the possible substitution of power for fuel is not, then, so far fetched as it might appear, and it has led to the building of a small electrically heated roaster with which it is hoped that some of these possibilities may be explored.

DISCUSSION

G. D. SCHOLL, Keokuk, Iowa.—I want to emphasize the point brought out: if solutions are absolutely pure, the tank-house troubles are very few. If you have one part in two million of antimony, you will have trouble, and lots of it, in the cell room; that is about the gage you might take of the degree of purity to which the electrolyte must be brought. Our investigations have not been exhaustive, as the plant with which I am connected is being dismantled. When we knew we were going

to dismantle, we ran a good many tests, doping the commercial cells with impurities, such as arsenic, cobalt, and nickel. Cobalt is very injurious and must be kept very low.

C. A. HANSEN.—I should like to call attention to one more matter, Leaching processes generally are assuming an increased importance, and they are sure to become much more important than they have been in the past. We have in this country large deposits of low-grade copper ores, such as that at Ajo. In general the surface portions of the ore-body are oxidized, the underlying ores are the original sulfides, and the intermediate ores contain both sulfide and oxidized copper minerals. So far leaching has been confined to the treatment of the oxidized surface ores with sulfuric acid. This treatment recovers little or none of the sulfide copper. On the other hand, present concentration methods applied to the mixed ores recover but little of the oxidized copper. It is therefore proposed to crush the mixed ore, leach out the oxidized copper, grind the leached tailings, and recover the sulfides by flotation. I believe that there is an excellent chance that we can make an 85 per cent. extraction of all of the copper in mixed ores of this coaracter by roasting and leaching them, and that the operating costs for such a process will not be as great as the costs of leaching followed by flotation. The development of such a process depends very largely upon working out proper roasting methods. It seems to me that the small electrically heated roaster which was used for the zinc-roasting experiments points to a readily available tool for exploring the copper-roasting problem.

E. H. HAMILTON,* Salt Lake City, Utah (written discussion).—There is a difference in the results obtained in roasting in a muffle, or single-hearth furnace, compared with results obtained when the hot ore drops from one hearth to another through a current of hot gas, as in the case of McDougall, Herreshoff, and Wedge furnaces. When dropping through the hot gases, there is an intensified action on the small particles, which flash up at an intense heat while the mass and relatively smaller surface exposure holds down the heat in the larger particle. Where iron is in close contact with the zinc, the tendency to form ferrite is greater in the very fine material, while the tendency to have unroasted zinc increases with the size of the particle.

In the grinding of ore in a dry tube mill without air separation, there is a marked difference in the proportions of the various sizes from the product obtained by wet grinding in closed circuit with a Dorr classifier. It is necessary to exercise good judgment in deciding the best procedure for grinding. It is not correct to screen out the various sizes of the leached product and have these analyzed and then assume that the size which

* Metallurgist, U. S. Smelting Co.

contains the higher per cent. of zinc is yielding less zinc. In some cases I found that the finest particles from the leached product ran high in zinc; but this was partly due to the fact that the finest material in the roasted product ran relatively high in zinc.

In all roasting operations, sizing of the particles is of the greatest importance. This is especially true of roasting mixtures of iron and zinc sulfides for zinc leaching, because the unroasted sulfide of zinc is not dissolved; and if ferrate of zinc is formed, each unit of iron renders 0.58 unit of zinc insoluble.

C. A. HANSEN.—As with many other new processes, certain advantages have erroneously been claimed for the electrolytic zinc process, erroneous at least in degree. In particular, it has been claimed that low zinc content ores can be advantageously treated directly by roasting and leaching. Many of the ores in this class are ferruginous; the majority of them can be concentrated by old and well established methods; and, in my opinion, concentration ahead of roasting and leaching will generally make for a better economic return than the direct roasting and leaching of the original total ore bulk. In either case, the ore must be crushed and ground; the concentrator expense, aside from the grinding costs, will generally be less than the roasting cost, per ton of material handled; the cost of roasters alone, when treating the entire ore bulk, will generally be greater than the combined cost of concentrator and roasters if the ratio of concentration materially exceeds 3 : 1. The extraction of zinc will ordinarily be as great for the combination of concentrator and zinc plant as it will be for the zinc plant alone, while the zinc plant costs will be diminished in many respects in proportion as the tonnage requiring treatment is diminished. In the west, practically all of the zinc ores carry valuable byproducts—gold, silver, lead, copper. These byproducts become available only through smelting processes. Their concentration in the original ore is seldom such as will permit sending the leach-plant residues to the smelter, while their concentration in the leach-plant residues resulting from the milled product will generally make it profitable to smelt those residues.

O. C. RALSTON (Niagara Falls, N. Y.).—I have noticed that, where ferrites are troublesome in the roasting of zinc ores, the extraction is usually very much lower than where they are not supposed to be present. I think that ferrites sometimes are blamed for some unroasted zinc for the reason that when ferrites do form, the temperature of roasting is usually maintained somewhat lower than is allowed where iron is not present in a form that produces ferrites. Grading the ore will, therefore, allow us to get the highest temperature conducive to good roasting without the formation of ferrites.

Mr. Hansen says that when roasting a ferruginous blend, it is much easier to form sulfate of zinc. It seems to me that this is fairly easily explained from the fact that iron oxide is the contact material very often used for making sulfuric acid, and from that angle, it seems very reasonable that marmatite ores should allow us to form a greater proportion of the zinc sulfate during roasting. I feel that marmatites are perhaps blamed for more than they might be. In my experience, the most extreme case of iron sulfide in solid solution with zinc sulfide—which constitutes marmatite —contained about 14 per cent of iron in the purest piece of the mineral that could be picked from the ore and was almost coal black. The same piece of mineral ore would contain, say, 54 per cent. of zinc.

The formula for ferrite of zinc would only call for about the equivalent weight of zinc on iron which, in this case, would be, say, 15 per cent. of zinc. In other words, if ferrite were the explanation of low extraction of zinc during leaching, the iron in that ore should have held back $^{15}/_{54}$ of the total zinc. Actually, it was impossible to roast the ore to leave only that amount of zinc behind, and you could always find some unroasted blende on grinding and mechanical separation in the laboratory, which seems to say that the formation of ferrites makes it impossible for us to roast it at a temperature which will allow complete desulfurization.

THE CHAIRMAN (E. P. MATHEWSON, New York, N. Y.).—The Anaconda Mining Co. has a plant that produces daily 150 tons of electrolytic zinc. The Consolidated Mining and Smelting Co. of Canada has a plant at Trail, B. C., that was producing regularly 30 tons of electrolytic zinc per day, but during the war the capacity was increased to double that. In Australia, they built one plant to produce 10 tons a day; that plant is so successful that they are going to increase it immediately to a capacity of 100 tons a day. There were several small plants in the United States. One was producing 7 to 8 tons of zinc per day. The war prices for high-grade zinc, of course, assisted a good deal in the development of the process. Now that the war prices are being modified and the demand for zinc temporarily lessened, the work is greatly curtailed.

DORSEY A. LYON, Washington, D. C.—As Mr. Hansen has brought out, we must look to hydrometallurgical processes to treat our ores. I believe that the day of the old-line treatment of those western ores is past. We will have to find a treatment for ore where we are far away from railroads, and under desert conditions, where we have no water, or have to contend with one kind of fuel; the electrolytic zinc is just one phase. Notwithstanding the great progress of the last few years, there will be greater progress in the treatment of these ores in the next decade.

C. A. HANSEN.—It has been said that the electrolytic zinc process is not a poor man's process. The criticism is a valid one. Aside from

the cost of the primary power station, the cost of a completely equipped electrolytic zinc plant may be taken at from $30,000 to $20,000 per ton per day of zinc capacity, as compared, for example, with something like $35,000 or $40,000 per ton of copper per day capacity for a large smelter and refinery treating fairly rich copper concentrates. I believe that, in respect to plant cost, the electrolytic zinc plant compares favorably with that of the alternative retort plant, whatever the scale of operations.

G. D. SCHOLL.—The plant at Keokuk was small, about 10 tons a day, but it was very successful. It is not being dismantled on account of failure but because it was decided not to build a commercial plant at this time. We had a peculiar plant; we treated fume entirely. A combination of fume and concentrates would be very good. We did not have time enough to develop as much of that work as we wished, but we did do a little with a combination of roasted Joplin ore and fume. The great difficulty in electrolytic zinc is the impurities. It is necessary to work to a very close limit and if roasted ore is combined with the fume, it is possible to dilute the impurities that come from the fume, and then by liberating certain portions of the solution every day, a happy medium may be obtained. There is much work to be done along these lines.

J. W. RICHARDS,* South Bethlehem, Pa.—I do not know exactly why the metallurgy of zinc in America has run toward the electrolytic method and in Europe toward the electrothermal. At present four plants in Norway, Sweden, and Finland are working on zinc ore by the electrothermal process and they are apparently prosperous. They have not taken up electrolytic methods at all. The reason may be their very cheap power. A furnace in southern Norway of 1000 kw. capacity is working on distilling zinc from zinc dross, possibly dross brought over from Germany. That furnace is operating with about 2000 kw.-hr. per ton, distilling the zinc at a cost of about $12 a ton. A very interesting side business was the distilling of an alloy containing 9 per cent. zinc and 4 per cent. copper, which was used for some purpose in Germany during the war. The zinc distilled over, leaving the aluminium-copper alloy, with lead and iron, for which they had found no use. Electric furnaces for working ore and distilling zinc have found a permanent place in the Scandinavian countries.

C. H. FULTON.—Are any details as to the type of furnace used in Norway, Sweden and Finland available?

J. W. RICHARDS.—At the present time, the companies are extremely secretive. They say they are working under the De Laval patents or some modification of them but will give no information as to the form of the furnace.

*Professor of Metallurgy, Lehigh University.

O. C. RALSTON.—It seems to me that the electrothermic extraction of zinc, when we know better how to operate it, will probably be better adapted to the small pocketbook. Mr. Allmand[6] describes a zinc distilling plant built during the war, or just before, in the Cologne area, which he investigated for the British Government. He describes a large, cylindrical furnace, 15 ft. in diameter by 15 ft. long with four electrodes at each end, and a smaller condenser with its end abutting on to the furnace proper. It was stated that a 77 per cent. recovery of zinc was made in this furnace during the war, with a zinc fume and zinc oxide charge, containing over 70 per cent. zinc. Until this recovery is improved, I do not think this furnace will compete with ordinary thermic zinc, but it seems to be a very promising kind of furnace and does not involve briqueting, with its endless troubles. Incidentally, the expense would be lower, as no particular preparation of the charge is necessary, whereas one of the papers read today describes an electrothermic zinc extraction process in which a highly involved briqueting, calcining, and handling treatment is used. These recent developments in electric zinc distilling lead me to feel that economic units of small capacity, united to the size of small pocketbooks, will soon be possible.

CHAIRMAN MATHEWSON.—I would like to modify the last speaker's statements to some extent. In the first place, the power required in the electrothermic treatment is about two and a half to three times as much as that for the electrolytic, so that power must be extremely cheap for that process to compete with the electrolytic method. Further, it has been found that for successful electrothermic treatment, a preliminary treatment must be given to the ore.

C. H. FULTON.—What power is required for electrolytic zinc?

CHAIRMAN MATHEWSON.—The power is calculated on the zinc produced from the solution; you can easily average 10 lb. per kilowatt-day by the electrolytic method, but only 4 lb. with the best electrothermic treatment. For days at a time, considerably over 12 lb. per kilowatt-day has been produced in some of the electrolytic plants.

C. A. HANSEN.—We have consistently made zinc under commercial operating conditions, but at current densities approximating 10 amp. per sq. ft., with as little as 2500 kw.-hr. direct current per ton of zinc cathodes. This, however, is not good economy by reason of the excessive cost of the low-current density electrolytic plant; 3000 kw.-hr. direct current per ton of cathodes is a perfectly practicable figure. The total power consumption for a reasonably large plant should not exceed 4000 kw.-hr. high-tension alternating current per ton of spelter actually

[6] A. J. Allmand and E. R. Williams: Some Chemical Plants in the Cologne Area. *Jnl.* Soc. Chem. Ind. (Aug. 15, 1919) **38**, 285.

shipped, this figure covering all power consumed in the zinc plant but not including power required for concentration.

Professor Fulton asked for power consumption reduced to the ton of 60-per cent. concentrates. It is right here that the basic difference between the retort process, or electrothermic process, and the electrolytic process comes in. The power consumption for the latter plant is practically independent of the grade of ore treated, and it is virtually 4000 kw.-hr. per ton of zinc output regardless as to whether that zinc is made from 60-per cent. zinc concentrates or from 25-per cent. zinc ores. On the other hand, with the thermic processes, the power consumption, the coal consumption, and in fact the costs as a whole, are practically the same for a ton of material treated, without regard to the zinc available from that ton of material.

GEORGE A. GUESS,* Toronto, Can. (written discussion).—On studying Mr. Hansen's figures I noticed the very high percentage of heat in his roaster gas, so having made balance sheets on roasters in which the figures were considerably less, I recalculated Mr. Hansen's problem. It is my opinion that the safest way to make a balance sheet is to actually calculate the heat in the gases and then leave the heat unaccounted for to heat lost by conduction, as figures for conduction and radiation are not very reliable.

Nearly every man has his own way of stating a heat balance. On smelter work I have always used the ton calorie, when weights were in tons of 2000 lb. The relation between cubic feet and ounces being the same as between cubic meters and kilograms simplifies calculations in English units.

My finding is that only 61.5 per cent. of the heat generated in the roaster is carried away in the furnace gases; this figure also compares with my previous experience.

HEAT SUPPLIED PER TON OF CONCENTRATES	TON-CALORIES
ZnS to oxide, 39.9 @ 89 @ 1700	604.0
ZnS to sulfate, 39.9 @ 1.78 @ 2850	20.8
PbS to sulfate, 3 per cent. @ 945	28.3
FeS_2 to oxide, 8.63 @ 3800	328.0
Arsenic sulfide to oxide, 0.3 per cent. @ 2230	6.7
Antimony sulfide to oxide, 0.3 per cent. @ 1420	4.3
CuS to CuO, 1 per cent. @ 1555	15.5
Total from concentrates	1007.1
Calories in coal	1350.0
Total per ton	2357.1

26.7 tons of concentrates, total per day, 63,000 ton-calories.

* Professor of Metallurgy, University of Toronto.

Gas per Day	Tons SO_2	Tons CO_2	Tons H_2O
Oxidation of zinc sulfide	9.32		
Oxidation of iron sulfide	5.27		
Oxidation of arsenic sulfide	0.10		
Oxidation of antimony sulfide	0.06		
Oxidation of copper sulfide	0.27		
Oxidation of carbon	....	13.35	
Oxidation of hydrogen	....	.....	2.66
Moisture in coal	....	.....	0.3
Moisture in concentrates	....	.....	0.8
Totals	15.02	13.35	3.76

At normal temperature and pressure the above weights would correspond to the following volumes in cubic feet.

	Cubic Feet
SO_2	168,200
CO_2	217,900
H_2O	149,800
	535,900

The only determined SO_2 in his furnace gas was 2 per cent. in test No. 3. Taking this figure, the total volume of gas will be 8,410,000 cu. ft. per day, and deducting the above total gives 7,874,100 cu. ft. per day of oxygen and nitrogen.

Heat in Furnace Gases per Day	Ton-calories
168,200 cu. ft. SO_2 @ 0.031 and 455° C.	1,185
217,900 cu. ft. CO_2 @ 0.0293	1,450
149,800 cu. ft. H_2O @ 0.0251	855
7,874,100 cu. ft. O and N @ 0.01967	35,200
Total heat in gases	38,690
Total generated	63,000
Percentage in gases	61.5

For conduction losses, I have taken a difference in temperature of 650° C., 18 in. of firebrick, K value 0.0042, which gives a heat loss for the furnace per minute of 22,000 pound-calories or per day 15,840 ton-calories. My heat balance then would be as follows·

	Ton-calories per Day	Per cent. Total
In calcines	3,220	5.1
Cooling water	4,350	6.9
Moisture evaporated	590	0.9
Conduction and radiation	15,840	25.1
Furnace gases	38,690	61.5
Unaccounted for	310	0.5
Total	63,000	100.0

C. A. HANSEN (author's reply to discussion).—I separated various screen portions and leached these separately. Each portion was analyzed both before and after leaching and I believe the conclusions reached regarding the relations between screen size, extraction, etc., are correctly reported. I feel, then, that I should escape Mr. Hamilton's criticism in this respect.

I agree with Mr. Ralston that the presence of iron in zinc concentrates probably has much to do with the formation of sulfate zinc. I tried to develop some definite relation between iron content and sulfate formation, but I did not succeed in finding a relationship that would stand my analysis.

There are several reasons for not accepting so simple a relationship as that which Mr Ralston proposes. Perhaps the most obvious is suggested by the behavior of two such dissimilar materials as the Bully Hill ore and the Butte Superior flotation concentrate during the latter stages of the roasting period. It is not impossible to roast a high iron-zinc concentrate, whether marmatite or otherwise, so as to eliminate practically all sulfide sulfur. The average sulfide-sulfur content of the calcines obtained at Bully Hill was not higher than 0.1 per cent. and it was often lower. Mr. Ralston may have tried to roast a coarse concentrate or to roast too quickly. I do not in the least doubt that zinc concentrates are often incompletely roasted in commercial practice, and that insoluble sulfide zinc is frequently charged improperly as ferrate zinc, but I do not agree that the presence of considerable iron will cause one to choose between ferrate formation and incomplete desulfurization.

I thoroughly agree with Mr. Guess that it would have been preferable to determine the volume of the roaster gases, and their heat content, in making up a roaster heat balance. Both my own heat balance, and that of Mr. Guess were, unfortunately *ex post facto* balances. Either could undoubtedly be much improved were the data collected with definite regard to composing a proper balance.

At the time my data were collected, we were trying to get a new plant into production and we naturally compromised considerably between expediency and thoroughness. We had no proper facilities for measuring gas volumes nor for accurately sampling the roaster gas. In fact, the reported sulfur-dioxide content meant little more to us than that it showed an ample supply of oxygen. On the other hand, I have considerable data covering the rate of heat dissipation of various surfaces maintained at various temperatures—data collected in connection with the design of electrically heated apparatus.

It was comparatively easy to measure the surface temperatures at various points on the roaster shell. Whatever inaccuracies may be

found in the reported balance sheet I doubt if the surface heat losses will be found very much in error. I am sorry that my files are not available since it might have been of interest to tabulate some of the data relative to surface temperatures versus surface heat losses. However, I think that some of these data have been published by Doctor Langmuir and by C. P. Randolph in the Transactions of the American Electrochemical Society.

Deterioration of Nickel Spark-plug Terminals in Service

BY HENRY S. RAWDON* AND A. I. KRYNITZKY,† WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

THE most commonly used material for terminals in spark plugs is commercial nickel wire, because of its relatively high temperature of melting, excellent heat conductivity, and slow rate at which the metal is oxidized, even upon continued heating at high temperatures. The grade commonly used for this purpose averages 97 per cent. nickel, the remainder being manganese, cobalt, iron, copper, with traces of other impurities always found in commercial nickel.

A peculiar and interesting type of deterioration that occurs in these nickel terminals during the service life of the spark plug was recently brought to the attention of the Bureau of Standards. Commercial spark plugs vary greatly in their size and shape and the terminals differ considerably as to their relative size, shape, number, and arrangement with respect to one another. Although this defect was studied in detail in only one form of spark plug, the deterioration is a characteristic of the material, *i.e.*, of nickel wire, rather than of the particular type of spark plug in which it was noted and studied. The mechanical features of the plugs, however, have a considerable bearing on the time required for the deterioration to become serious. The results of this study of the deterioration of nickel terminals in service should be of value to the makers of all types of spark plugs in which the terminals are made of this metal.

CHARACTER OF DETERIORATION OF WIRES DURING SERVICE

Macroscopic Appearance and Properties of Changed Wire.—The nickel terminals in which the deterioration was studied were taken from spark plugs having a central terminal with the ground or side terminals attached firmly at both ends to the shell of the plug. In some of the plugs, two side terminals were used, one on each side of the central one. Although both terminals were found to have deteriorated to some extent, the attack of the central one was quite negligible compared to that of the side ones. These latter wires had developed, in service, transverse cracks that, in many cases, were as sharp and definite as a knife-cut. After a separation occurred, the breach widened by loss of material from the

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† Assistant Physicist, U. S. Bureau of Standards.

ends of the fractured wires until a gap of as much as 1 cm. often resulted. Fig. 1 shows the appearance of some of the side terminals in different stages of deterioration. In Fig. 2 is shown the appearance of the sur-

a *b*

FIG. 1.—END OF SPARK PLUGS, NATURAL SIZE, SHOWING FRACTURE IN SIDE TERMINALS. *a* AND *b* REPRESENT DIFFERENT GRADES OF WIRE.

face of the side terminals after the removal of the carbonaceous deposit that usually covers them. The surface is roughened by a series of parallel

FIG. 2.—SURFACE OF SIDE TERMINAL AFTER CONSIDERABLE SERVICE, SHOWING TRANSVERSE CRACKS THAT DEVELOP. × 3.

transverse cracks; none of these, however, have penetrated deeply enough to cause a break of the wire. In general, these transverse cracks occur more frequently on the side of the terminal on which most of the sparking

occurs, that is, the one facing the central terminal, than on the farther side. The central terminal shows no appreciable change other than a slight roughening of the tip.

The appearance of the fracture of the side terminal is that of very brittle material, there being no elongation and no reduction of cross-sectional area. The face of the fracture itself is rough and crystalline. The mechanical properties of three samples of new wire, said by the manufacturers to be of the same stock as the terminals that failed, were determined with the results given in Table 1.

TABLE 1.—*Mechanical Properties of Nickel Wire*

Number of Specimen	Character of Wire	Ultimate Strength, Lb. Per Sq. In.	Elongation, Per Cent.	
			In 8 in.	In 2 in.
1	Hard drawn	110,000	not determined, very small	
2	Annealed	73,000	26	30
3	Annealed	78,500	29	31
4	Annealed	65,200		28

Specimen 1 was said to be the material from which the used terminals shown at *a* Fig. 1 were made and resembles it quite closely, see Table 2. The terminals shown at *b*, which were said to have been made from wire similar to specimens 2 and 3, evidently were made from wire quite similar in composition to specimen 4, see Table 2, though not necessarily of the same mechanical properties. Specimen 4 is a sample of annealed nickel wire from the Bureau of Standards stock; this material was used in all the experimental work described later.

The fragments of the deteriorated wire terminals removed from the spark plugs were found on the whole to be rather ductile and to stand several sharp right-angle bends before breaking. The extreme end portion immediately adjacent to the break, however, was brittle and broke readily when an attempt was made to bend it. An explanation of the embrittlement of nickel wires used for the winding of an electric furnace, offered by Carpenter,[1] assumes the presence of occluded gas within the metal, which is liberated under the combined action of electricity and heat. The wires described by Carpenter separated into a bundle of long thin threads after considerable use of the furnace. The explanation does not answer in the present case, in which the wires are always fractured by a series of transverse cracks.

Both the deteriorated terminals and samples of unused wires were analyzed chemically; the results are summarized in Table 2.

[1] H. C. H. Carpenter: National Physical Lab., *Collected Researches* (1908) **3**, 97.

TABLE 2.—*Chemical Composition of Commercial Nickel Wire*

Specimen	Nickel, Per Cent.	Cobalt, Per Cent.	Copper, Per Cent.	Silicon, Per Cent.	Manganese, Per Cent.	Iron, Per Cent.
a Used wires	97.3[a]		0.10	0.40	1.50	0.5
a Fig. 2	97.2[a]		0.10	0.40	1.50	0.5
b Used wires	99.0[a]		0.10	0.40	0.05	0.4
b Fig. 2	99.1[a]		0.10	0.40	0.05	0.4
c No. 1, Table 1	97.1	0.7	0.14	0.12	1.30	0.6
d No. 2, Table 1	96.9	0.3	0.09	0.25	1.60	0.8
e No. 3, Table 1	97.1	0.3	0.09	0.18	1.50	0.8
f No. 4, Table 1	98.1	1.1	0.18	0.07	0.20	0.3

[a] Cobalt was not determined, it is included with nickel.

It will be noted that deterioration occurs in both the usual "97 per cent. grade" of nickel wire with relatively high manganese content and in the wire of higher nickel content.

Microstructural Features.—In Fig. 3 is shown the microstructure of commercial nickel wire in the hard-drawn and in the annealed states (specimens 1 and 4, Table 1, respectively). The metal consists of but one type of crystals, as is true with pure metals and solid solutions in general. In the hard cold-drawn wire, the crystals show the results of the severe distortion due to the drawing, by their elongated form; upon annealing sufficiently, a recrystallization takes place and the characteristic appearance shown in *b* results. The minute inclusions of oxide and other impurities, which have been arranged in lines parallel to the direction of working during the drawing operation, have been dissolved by the strong etching solution (concentrated nitric acid), which is necessary to develop satisfactorily the crystalline structure of nickel; a definite etching pit marking the location of each inclusion results. At *c* is shown the outer surface of the annealed nickel wire of *b*. This wire has received no treatment after the final annealing by the manufacturers. In an extremely thin outer layer, a structural change very similar to that which occurs in the nickel terminals during service has taken place. This undoubtedly occurred during the final annealing, the hard-drawn wires showed no trace of such a change in the surface metal. In the following discussion of structural changes produced experimentally in the nickel wire, it should be borne in mind that the extreme surface layer has been changed already to the extent shown in *c*.

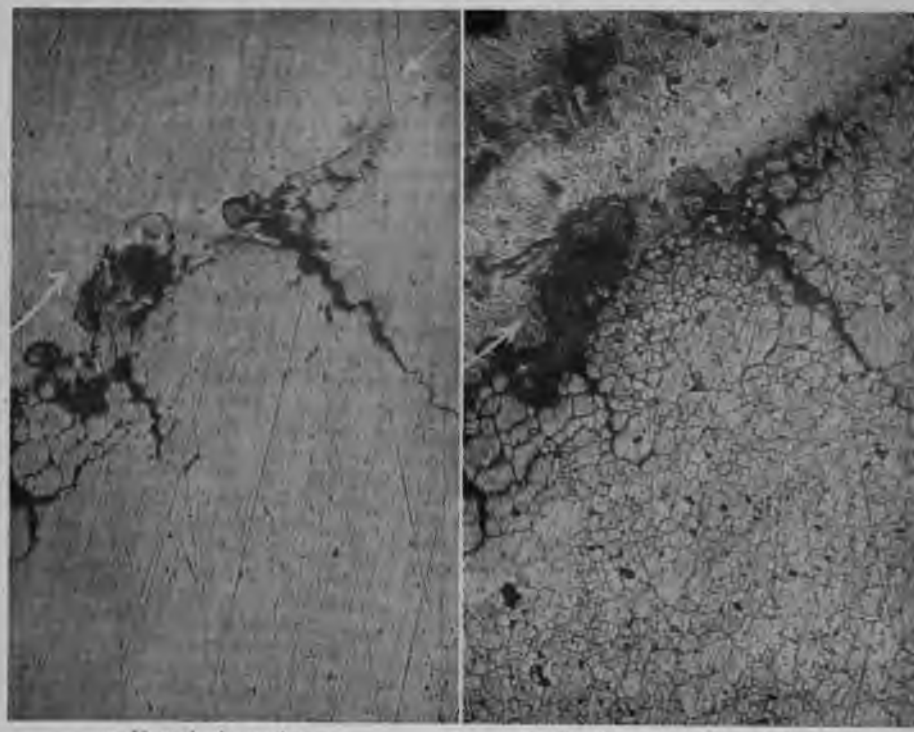
Longitudinal sections of the deteriorated side terminals were prepared for microscopic examination. The small fragments of the wire were plated with a heavy deposit of electrolytic copper to preserve the edges of the section during the process of polishing; the coated piece was then mounted in a suitable matrix and the resulting composite specimen sectioned and polished. In most of the photomicrographs a part of the

a. Longitudinal section of hard-drawn wire.

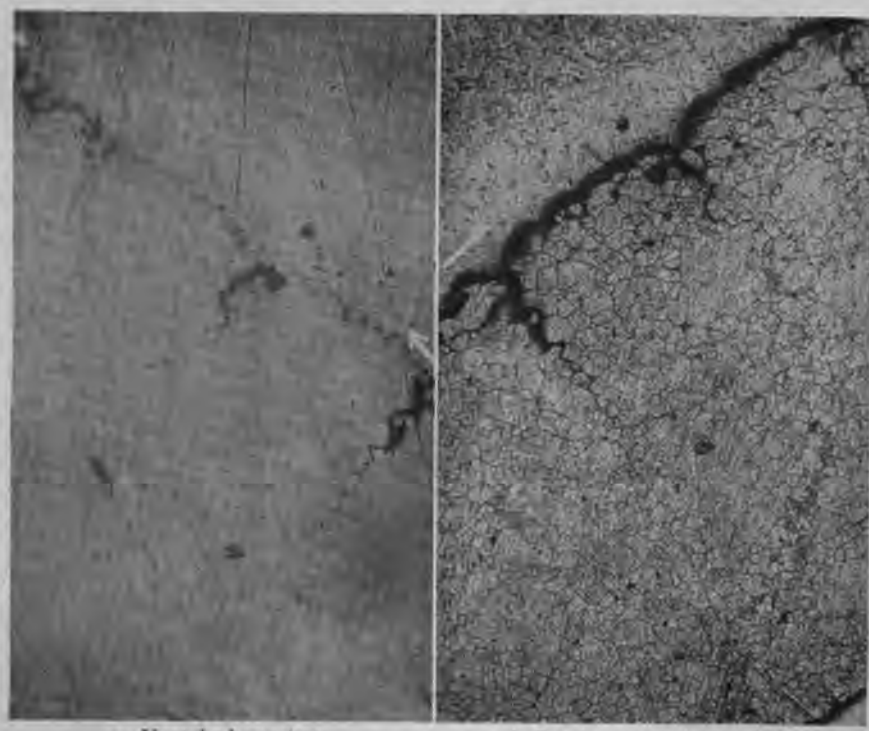
b. Longitudinal section of annealed wire.

c. Edge of section shown in *b*., *i.e.*, surface of wire. Intercrystalline fissures appear in very thin surface layer of metal, probably formed during final annealing of wire.

FIG. 3.—MICROSTRUCTURE OF WIRE OF GRADE USED AS SPARK PLUG TERMINALS.
ETCHING, CONCENTRATED NITRIC ACID, 5 SEC. × 500

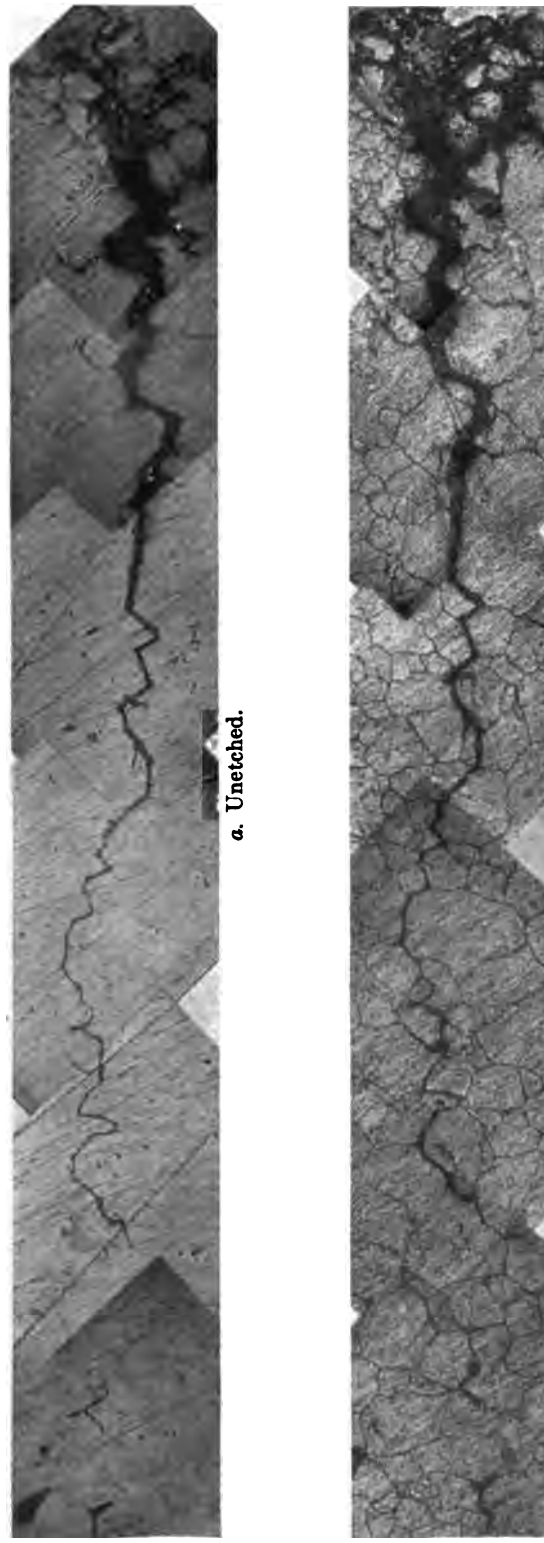


a. Unetched specimen. *b*. Specimen *a* after etching.



c. Unetched specimen. *d*. Specimen *c* after etching.

FIG. 4.—LONGITUDINAL SECTIONS OF SIDE TERMINALS SHOWING DETERIORATION IN SERVICE. ARROWS INDICATE EDGE OF NICKEL WIRE. ETCHING, CONCENTRATED NITRIC ACID, 1 TO 2 SEC. × 100.



a. Unetched.

b. Etched, 1 to 2 sec., with concentrated nitric acid.

FIG. 5.—LONGITUDINAL SECTION OF A SIDE TERMINAL, SHOWING TRANSVERSE CRACK.
× 250.

protective layer of copper appears immediately adjacent to the edge of the section of the wire.

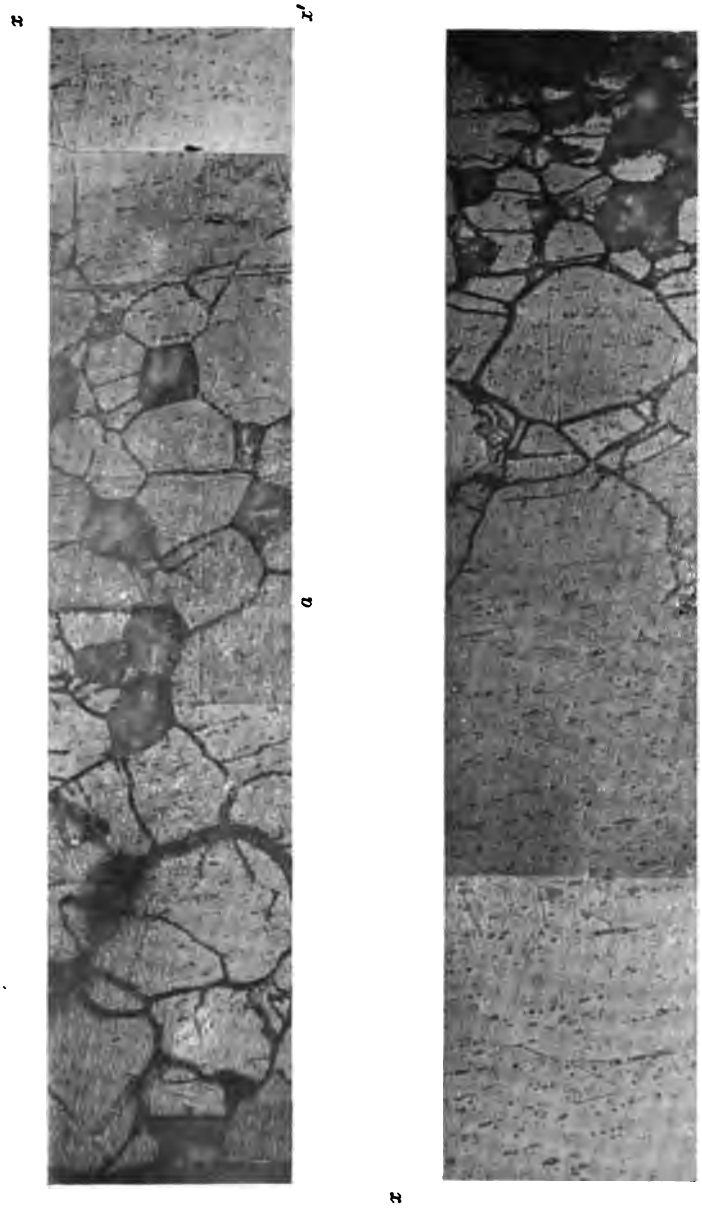
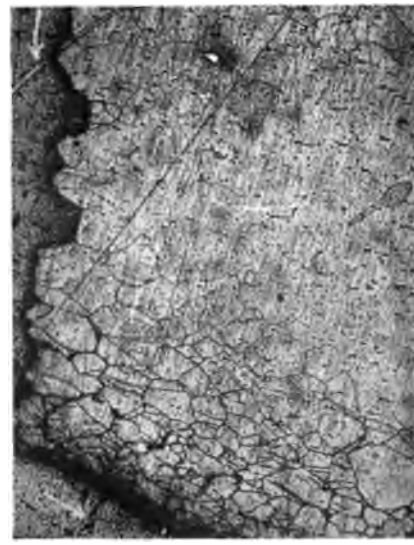


FIG. 6.—MEDIAL LONGITUDINAL SECTION THROUGH NICKEL SIDE TERMINAL OF SPARK PLUG AFTER DETERIORATION. THE TWO MICROGRAPHS SHOULD BE FITTED TOGETHER ALONG $x-x'$. ETCHING DEVELOPED INTERCRYSTALLINE FISSURES IN OUTER LAYERS; SOME CRYSTALS HAVE LOOSENED AND DROPPED OUT OF PLACE. ETCHING CONCENTRATED NITRIC ACID, 5 SEC. × 250.

In Fig. 4 is shown the appearance of longitudinal sections of the side terminal. A series of parallel transverse cracks, some of which extend very deeply into the otherwise sound metal, is apparent in the unetched specimen. By etching with concentrated nitric acid for several seconds,

the crystal boundaries of the metal are revealed and the intercrystalline nature of the transverse cracks is made evident. Fig. 5, *a* and *b*,



a. Network in outer zone of wire and also intercrystalline fracture. × 150.

b *c*

b and *c* show lower left-hand corner before and after etching. Some intercrystalline fissures show a gray non-metallic substance, evidently oxide. Etching, concentrated nitric acid, 1 to 2 sec. × 375.

FIG. 7.—LONGITUDINAL SECTION THROUGH FRACTURED END OF WIRE.

shows the course of one of these cracks at a relatively high magnification.

In addition to the intercrystalline transverse cracks that penetrate deeply into the metal, the microscopic examination revealed a zone on the outside of the wire in which the crystal boundaries etch very readily, forming a complete network of intercrystalline fissures; in some cases entire crystals become detached in this zone and fall bodily out of place. These features are shown in Fig. 6, which gives a narrow transverse section entirely across one of the side terminals.

In Fig. 7 is shown a part of one of the side terminals adjacent to the fracture that occurred in this wire. The break was distinctly intercrystalline, as is to be expected from the nature of the transverse cracks. Before etching, many of the intercrystalline fissures are seen to contain a

FIG. 8.—LONGITUDINAL SECTION OF A SIDE TERMINAL DETERIORATED IN SERVICE, UNETCHED. EUTECTIC-LIKE NETWORK FORMS BETWEEN CRYSTALS IN OUTER ZONE OF WIRE. ARROWS INDICATE EDGE OF SECTION OF WIRE. × 500.

film of gray non-metallic substance. This is shown in *b* and *c*. In Fig. 8, the intercrystalline eutectic-like network, in the outer parts of the deteriorated wires, is shown; this appears in the unetched specimen. Fig. 9 shows a section through the fracture of one of the broken side terminals and clearly shows the intercrystalline path of the fracture together with some of the sound unchanged metal just back of the face of the break.

The examination of the central terminal showed that a change of the same general character as occurred in side terminals had taken place in this one also, but to a very much less extent. In a zone of metal that covers the upper end of the terminal like a cap, the intercrystalline network is well developed. This cap was found in some terminals to be

approximately 0.3 mm. (0.012 in.) thick at the tip and to extend as a layer of constantly decreasing thickness for approximately 15 mm. (⅝ in.) along the length of the terminal. In the same specimen the side terminal had fractured and a gap of over 7 mm. width had formed. In Fig. 10, the general extent of the deterioration of the central terminal is shown; in no case were there found any of the definite transverse

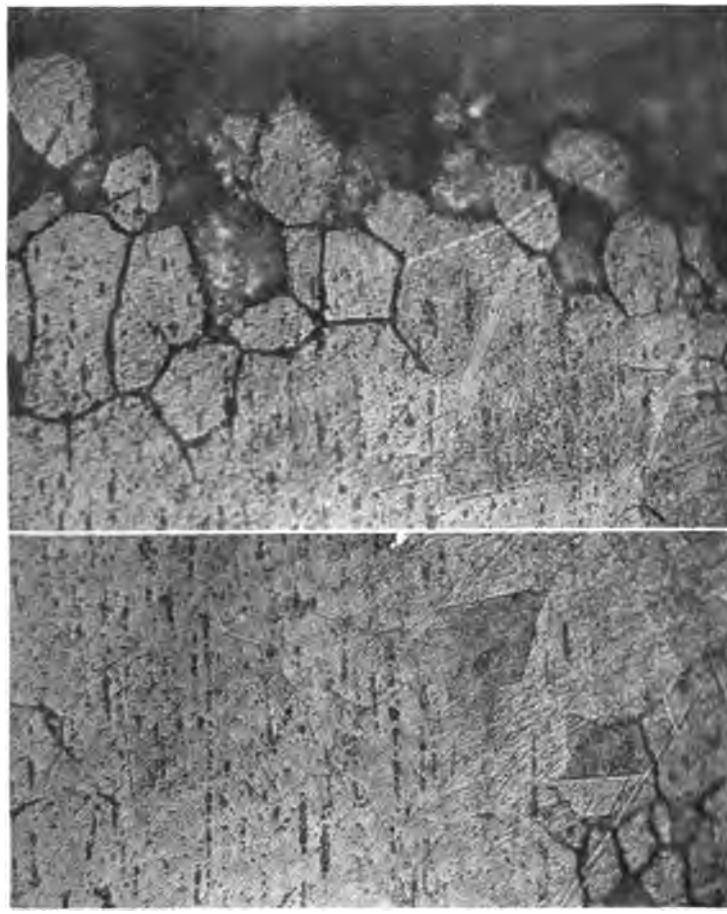


FIG. 9.—LONGITUDINAL SECTION THROUGH FRACTURED END OF BROKEN TERMINALS. PATH OF FRACTURE IS TRULY INTERCRYSTALLINE; UNCHANGED SOUND METAL APPEARS JUST BACK OF BREAK. ETCHING, CONCENTRATED NITRIC ACID FOR 5 SEC. × 500.

cracks noted in the side terminal. Tiny fissures gradually form in the attacked metal that caps the end of the terminal, and small fragments become detached, thus gradually shortening the terminal. The relative intensity of the attack in the central and in the side terminals is shown in Fig. 11. A section of a cross-section of the top of the central terminal, the fractured end of a side terminal and the cool end of the same fragment,

that is, the end attached to the shell of the plug, shows the depth of the zone of deterioration in each case.

To illustrate the service behavior of side terminals anchored at only one end, a number of spark plugs of a different type used for various periods in a Liberty engine were examined. The side terminals in this

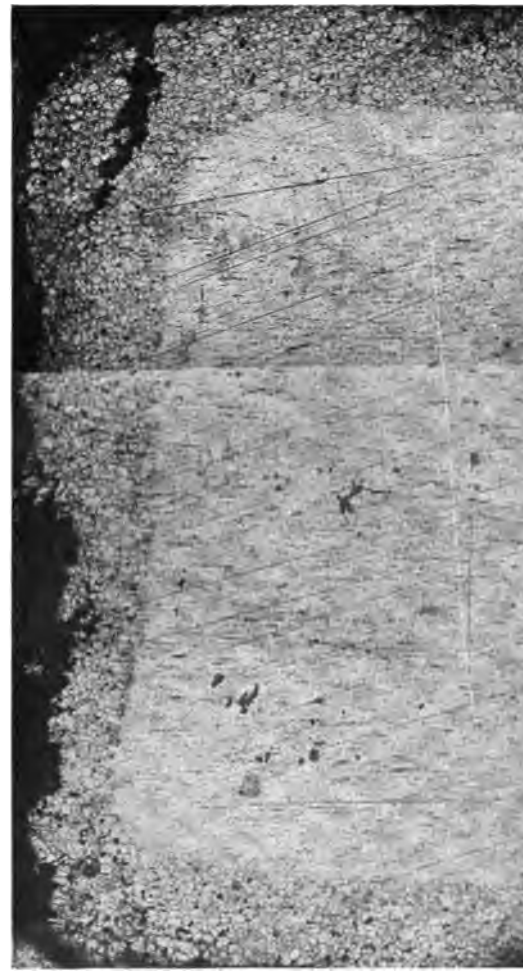
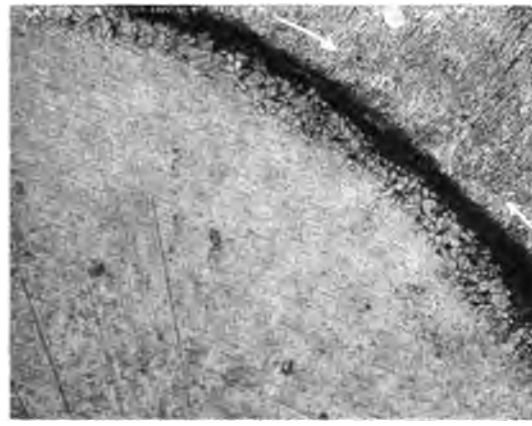


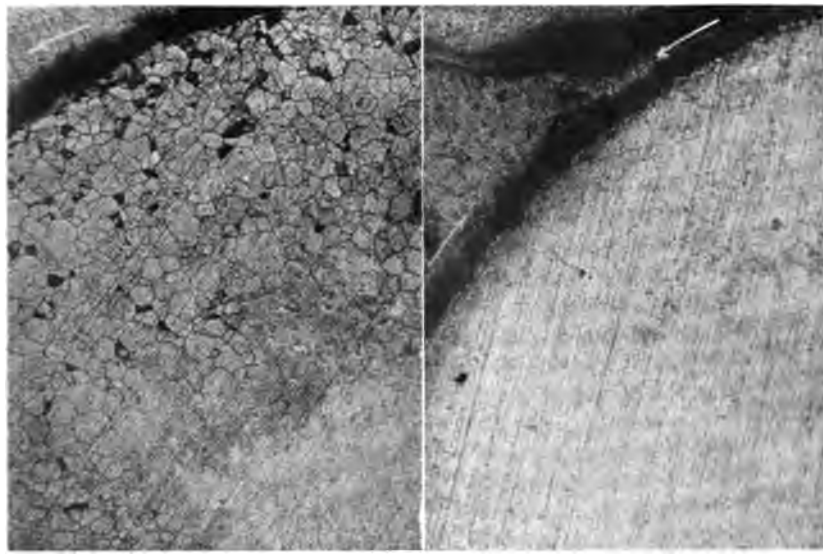
FIG. 10.—LONGITUDINAL SECTION THROUGH TIP OF CENTRAL TERMINAL TO SHOW EXTENT OF DETERIORATION. THIN LAYER THAT ENTIRELY CAPS UPPER END HAS BEEN AFFECTED. ETCHING, CONCENTRATED NITRIC ACID, 1 TO 2 SEC. × 55.

plug are bent at a right angle, fastened to the shell at one end, and terminate near the tip of the central terminal, which is of nickel wire of the same size as the side terminals. Both terminals show the same type of deterioration as was found in the central terminals of the plugs previously examined, that is, a cap of metal in which the intercrystalline fissures are

well developed covers the free end of each. Fig. 12, *a* and *b*, shows the appearance of the two. In none of the terminals, side or central, were any of the deep transverse cracks found. The plugs had been subjected



a. Portion of cross-section of upper tip of central terminal.

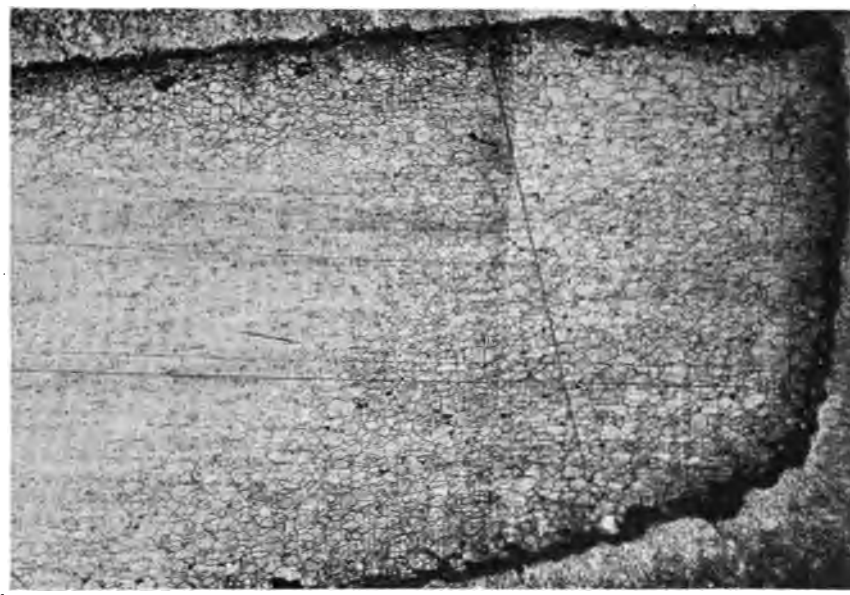


b. Portion of cross-section just back of fracture of side terminal.

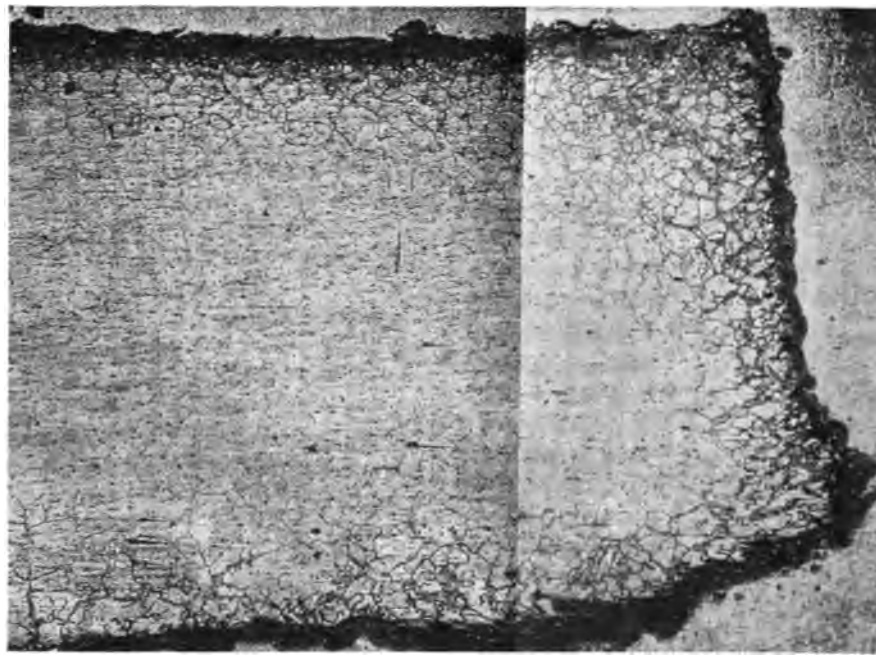
c. Portion of cross-section of opposite end of *b*, *i.e.*, where terminal is attached to plug casing (cool end).

FIG. 11.—RELATIVE DETERIORATION OF CENTRAL AND SIDE ELECTRODE. CENTER OF WIRE CORRESPONDS QUITE CLOSELY IN EACH CASE WITH LOWER CORNER OF PHOTOMICROGRAPHS. × 75.

to a continuous service, which varied in the different plugs from 9¾ to 28 hr. The thickness of the zone of deteriorated metal in the terminals that had the longest service does not differ markedly from that of the



a. Longitudinal section of free (hot) end of side terminal.



b. Longitudinal section of tip of central terminal.

FIG. 12.—TERMINALS FROM SPARK PLUGS IN WHICH SIDE TERMINAL IS ANCHORED AT ONE END ONLY, REMOVED AFTER 9 HR. SERVICE IN LIBERTY MOTOR. ETCHING, 2 SEC. IN CONCENTRATED NITRIC ACID. × 55.

terminals of the shorter service. The loss of surface metal from the tip of the wires during service in part explains the rather striking uniformity in thickness of the cap of deteriorated metal.

Possible Factors Contributing to the Deterioration

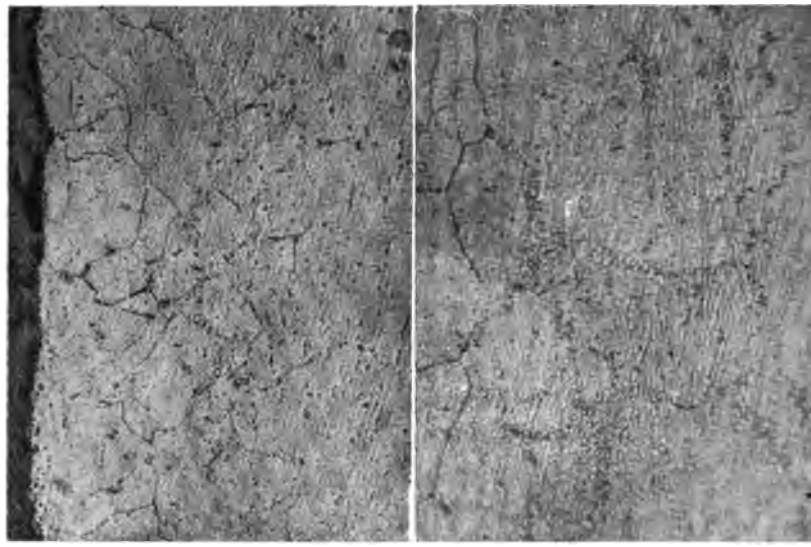
Chemical Composition.—From the results of Table 2, it is evident that variations in chemical composition, such as occur in commercial nickel wire, are not a determining factor in the deterioration of the wire in service. Terminals of nickel of relatively high purity (for commercial wire) were found to be attacked in the same manner as those of lower nickel content. Wires in which the manganese content was purposely left rather high appear to behave the same in service as those in which the minimum amount of manganese for controlling the sulfur content has been used in the metallurgical operations previous to casting. It was found possible, as described later, to experimentally reproduce the same type of deterioration in nickel wire (specimen *f*, Table 2) in which the impurities were, in general, less than those of any of the wires that deteriorated in service.

Oxidation.—In order to determine the part played by oxidation in the development of the intercrystalline network of fissures by which the material is embrittled, specimen 4, Table 1, several wires were heated at a high temperature for periods of several days by being suspended in a small tube furnace of the resistance type. The ends of the tube were loosely plugged with asbestos to prevent convection air-currents, which interfere in maintaining the temperature desired, but no other precautions were taken to exclude the air, see specimens 3*a*, 4*a*, and 12*a*, Table 3. In Fig. 13 are shown the structural changes produced by heating for 120 hr., 48 hr. at approximately 750° C. (740°–768°), and 72 hr. at approximately 870° C. (862°–882°). A very slight etching, 1 sec. in concentrated nitric acid, is necessary to show properly the changes that have occurred. The thick oxide coating that forms has a very smooth shining surface resembling varnish; it is very adherent to the metal beneath. On the inner side of this black oxide layer there is a thin film of green material. This layer, according to Burgess and Foote,[2] is probably nickelous oxide, Ni_2O, the thick outer layer being nickel oxide, NiO. In the outermost portion of the metal, immediately adjacent to the oxide layer, an intercrystalline eutectic-like network has formed. Microscopic examination at high magnification shows that this network on the inner side, that is, toward the center of the wire, of the zone in which it has formed, consists of discrete particles, probably of the nickelous oxide, which

[2] G. K. Burgess and P. D. Foote: U. S. Bureau of Standards, *Sci. Paper* 224, 53.

dissolve very readily in the etching fluid, leaving definite etching pits. The appearance of the granular network is that of a eutectic. Without doubt

a. × 75.



b. × 375. *c*. × 750.

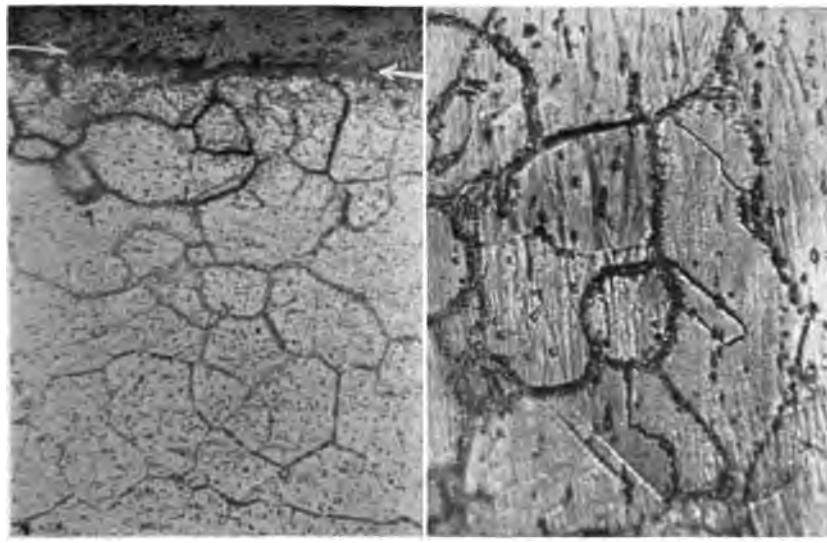
FIG. 13.—LONGITUDINAL SECTION OF SPECIMEN 12*a*, TABLE 3, HEATED 120 HR.; 48 HR. AT APPROXIMATELY 750° C., 72 HR. AT APPROXIMATELY 870° C. DEFINITE EUTECTIC-LIKE INTERCRYSTALLINE NETWORK HAS FORMED IN METAL JUST BENEATH THE HEAVY OXIDE LAYER. NETWORK AS IT FIRST FORMS IS GRANULAR IN APPEARANCE, LATER COMPLETE FILM IS FORMED. ETCHING, 1 SEC. IN CONCENTRATED NITRIC ACID.

this network indicates the manner in which the oxidation progresses into the solid metal. A similar tendency of steels of a rather high nickel

content to oxidize selectively along the boundaries of the crystals has been pointed out by Stead.[3]

A series of heating and cooling curves were taken to illustrate the behavior at high temperatures of nickel that had been oxidized by heating

a. × 75.



b. × 375. *c.* × 750.

FIG. 14.—SAME MATERIAL AS FIG. 13, ETCHED DEEPLY. GRANULAR EUTECTIC-LIKE NETWORK HAS DISSOLVED LEAVING NUMEROUS ETCHING PITS AT CRYSTAL BOUNDARIES. ETCHING, CONCENTRATED NITRIC ACID FOR 8 SEC.

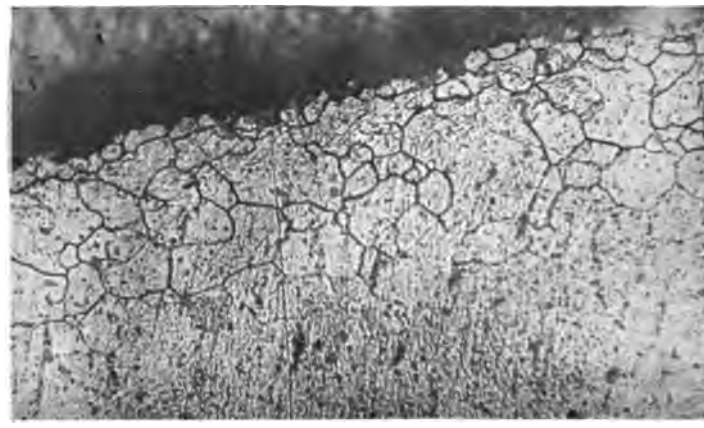
for 120 hr. as given above. No evidence was obtained in the behavior of the metal as recorded in the heating and cooling curves that the eutectic-

[3] J. E. Stead: *Jnl.* Iron and Steel Inst. (1916) **44**, 243.

like network fuses within the temperature range 500° to 900° C.; although it is formed at a temperature considerably below the upper limit given. The heating and cooling curves obtained were identical with those of the same material before oxidizing.

As the oxidation progresses, the isolated particles of the eutectic coalesce and a continuous film is formed, as is to be seen in the outer portion

a. Cross-section (unetched) of the heated portion.



b. Similar cross-section, etched 5 sec. in concentrated nitric acid.

FIG. 15.—EFFECT OF A REDUCING ATMOSPHERE (CARBON MONOXIDE) ON NICKEL WIRE HEATED FOR 5 HR. IN CARBON MONOXIDE AT 720° C. × 500.

of the zone of the intercrystalline network, *b*, Fig. 13. In Fig. 14, the same material is shown after deeper etching, the appearance of the structure is identical with that of the terminals that have deteriorated in service. Upon long continued heating, the width of this zone of intercrystalline network widens and a considerable embrittlement of the wire results.

Long continued heating also increases the crystal size of the metal very materially and thus adds to the weakness of the overheated metal. In none of the wires that were heated was it possible to produce the definite transverse intercrystalline cracks, such as were found in the deteriorated terminals and by which the fractures are caused. It would appear that

a. Cross-section of heated portion of wire unetched; a thin brittle layer, probably carbide, formed on surface.

b. Similar cross-section, etched 5 sec. in concentrated nitric acid.

FIG. 16.—EFFECT OF REDUCING ATMOSPHERE (ACETYLENE) ON NICKEL WIRE HEATED FOR ABOUT 3 HR. AT 980° C. GAS WAS PASSED OVER THE HOT WIRE INTERMITTENTLY AND HEAVY DEPOSIT OF CARBON FORMED. × 100.

continued heating in the presence of air at a high temperature contributes to the embrittling of the material. The effect of oxidation is very slight, however, compared with that of some of the other possible contributing causes and may probably be disregarded as one of the causes of the embrittling of the wire when used in a spark plug.

Reducing Atmosphere.—The effect of a strongly reducing atmosphere upon hot nickel wires was determined by heating wires, in carbon monoxide and in acetylene; specimen 4, Table 1. The carbon monoxide was prepared by the action of concentrated sulfuric acid upon sodium formate and passed through soda lime to remove any carbon dioxide that might be present. Carpenter and Smith have shown that carbon dioxide in any appreciable amount will inhibit the carburization of iron by means of carbon monoxide.[4]

The effect of carbon monoxide was determined at two temperatures. In the first case, 710°, the gas was passed at a very slow rate continuously over the wire, which was contained in a long silica tube electrically heated at the center for 5 hr. In the second case, the furnace was maintained at 980° C. and the gas was passed intermittently, the furnace being tightly

FIG. 17.—LONGITUDINAL SECTION THROUGH SPOT PRODUCED UPON SURFACE OF NICKEL WIRE BY ELECTRIC SPARK. IN ZONE 1, METAL HAS BEEN HIGHLY HEATED; INTERCRYSTALLINE NETWORK PRODUCED EXTENDS INTO ZONE 2, THE SOUNDEST METAL WHICH HAS REMAINED RELATIVELY COOL. ETCHING, CONCENTRATED NITRIC ACID FOR 3 SEC. × 500.

closed at both ends when the gas was not passing; the specimen was exposed to the hot gas for 4 hr. In both cases carbon dioxide was produced, as was shown by the escaping gas as it bubbled through barium hydroxide but no pronounced deposit of carbon on the wire was formed. The effect of the gas on the nickel is essentially the same in the two cases. Fig. 15 shows the appearance after the treatment. No change was apparent in the unetched state, slight etching reveals a thin surface layer in which the intercrystalline fissures are well developed.

The specimen that was exposed to acetylene was heated at 980° C. for approximately 3 hr. A very heavy deposit of carbon was produced

[4] H. C. H. Carpenter and C. C. Smith: Reaction Between Carbon Monoxide and Electrolytic Iron. *Jnl.* Iron and Steel Inst. (1918) **98**, 139.

in this case and it was not possible to pass the gas through continuously. The surface of the wire became coated with a thin black brittle coating, which flaked off on slight bending, leaving the surface roughened. Undoubtedly this layer is a carbide. Fig. 16 shows the change produced in the wire by the hot acetylene. The wires were still ductile after heating, in both cases, and gave no evidence of pronounced brittleness upon bending.

The effect of the hot reducing gases appears to be somewhat greater than that of an oxidizing atmosphere, although the method of attack is the same in each case, that is, intercrystalline. No indications of localized action, which might result in deep transverse cracks in the wire, were observed in any of the wires exposed to the reducing gases; the metal is uniformly affected at the exposed surface.

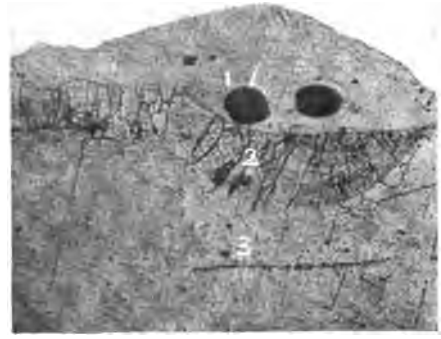
Intense Local Heating.—In general, the effect of the electric spark on the terminal must be regarded as an intense local overheating. Two nickel wires, specimen 4, Table 1, were used as electrodes and sparks passed between them. The sparks were produced by breaking the secondary circuit of a transformer (an "electric-stylograph" used for writing on metals, was used). The current in the secondary winding could be varied from approximately 100 to over 300 amp. These conditions, of course, are not comparable with the ignition system of the engine. It was not attempted to duplicate service conditions, but rather to accelerate the action. The aim, however, was to strongly heat the metal in a very small area while the remainder remained relatively cool. Specimens were prepared by sparking in air and also in an atmosphere of carbon dioxide, in order that oxidation might be reduced to a minimum. The results obtained in both cases were of the same general character.

In Fig. 17 is shown the appearance of a spot produced by a relatively weak spark. The part that has been heated strongly is sharply differentiated from the metal that remained rather cool. A network of intercrystalline cracks has broken up the continuity of the overheated metal; these extend for some distance into the surrounding sound metal as intercrystalline fissures.

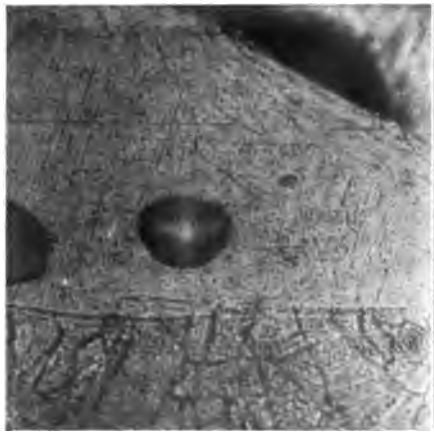
A much larger overheated area is shown in Fig. 18. This specimen was sparked in an atmosphere of carbon dioxide, a much heavier current being used. Three zones are to be noted; an outer one in which the metal was fused, an intermediate one that was strongly overheated and developed the network of intercrystalline fissures, and the inner or relatively cool metal, which is unchanged for the most part except for the intercrystalline cracks of the overheated zone that extend into it. The distinct dentritic pattern of the metal in the outer zone is proof that the metal here has solidified from the molten state with the production of this characteristic structural pattern. The line of demarcation between the overheated (but not melted) metal and the relatively cool portion is

very definite. The intercrystalline cracks have, however, extended into the sound metal of the interior; they are truly intercrystalline in their course.

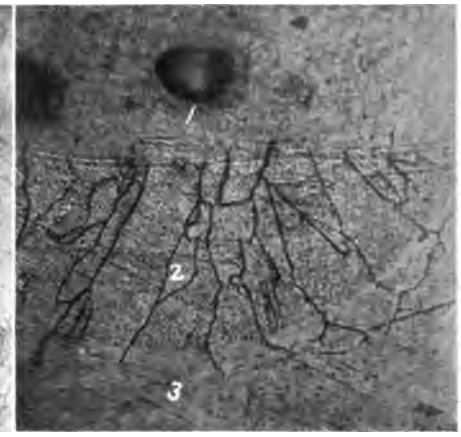
In none of the wires heated by the electric spark could any of the definite transverse cracks be found, although in some cases the effect of as many as 25 to 30 sparks was concentrated in a narrow ring around the wire. The intercrystalline network produced by the local heating by



a. × 100. Three distinct zones are seen.



b. × 375. Zone 1 of *a*. Metal has been melted and, on solidification, produced the characteristic dendritic structure.



c. × 375. Zone 2 of *a*. Metal has been highly heated but not melted. Intercrystalline network produced extends into Zone 3 of *a*, the sound metal which remained relatively cool.

FIG. 18.—LONGITUDINAL SECTION THROUGH SPOT PRODUCED ON SURFACE OF NICKEL WIRE BY ELECTRIC SPARK IN ATMOSPHERE OF CARBON DIOXIDE.

the electric spark is properly to be regarded as a heat effect only and is not accompanied by oxidation, except in the outermost surface of those produced in air.

Influence of Combined Action of Tensional Stress and Heat.—In order

to explain the formation of the definite transverse cracks that form in the side terminals, a series of wires were stressed in tension while heated at a high temperature; specimen 4, Table 1. No attempt was made to reproduce the temperature of the terminals in service, since no accurate measurement can be made of the temperature of the small spot at which the spark occurs; the measured temperature of the terminal would be considerably below the actual temperature at this spot. The temperatures used below and elsewhere are considerably above the average service temperature of the terminal. The work of Rosenhain and Ewen[5] has shown that the fracture produced in metals broken in tension while hot is always intercrystalline in its course. The samples of wire tested were about 2 ft. in length; the specimen was inserted through a small vertical tube furnace of the resistance type, firmly attached to a support above and loaded with a weight below. Only the central part of the wire was heated; in all cases the break took place within this heated portion. The results are summarized in Table 3.

TABLE 3.—*Combined Effect of Heat and Stress on Nickel Wires*

Specimen Number	Average Temperature, Degrees C.	Load, Lb. Per Sq. In.	Results and Remarks
1	942	3300	Wire put in cold furnace, gradually heated, broke in 3 hr.
2	970	3800	Put in cold furnace, gradually heated, broke in 3 hr., 50 min.
3	940	3300	Put into hot furnace, broke in 20 min.
3[a]	940	no load	Heated continuously for 72 hr.[a]
4	940	3800	Put into hot furnace, broke in 20 min.
4[a]	940	no load	Heated continuously for 72 hr.[a]
5	988	3800	Put into hot furnace, broke in 10 min.
6	993	3300	Put into hot furnace, broke in 13 min.
7	993	3500	Put into hot furnace, broke in 12 min.
8	1004	3300	Put into hot furnace, broke in 13 min.
9	1020	3300	Put into warm furnace, heated rapidly to temperature, wire broke in 30 min.
10	1100	1180	Wire broke, time not determined as wire broke during night.
11	740	1180	Heated 72 hr., wire did not break.[a]
12	740 880	1180	48 hr. at lower temperature, 72 hr. at higher, wire did not break.[a]
12[a]	740 880	no load	48 hr. at lower temperature, 72 hr. at higher.[a]

[a] Microexamination showed the beginning of an intercrystalline network.

[5] W. Rosenhain and D. Ewen: Intercrystalline Cohesion in Metals. National Physical Lab., *Collected Researches* (1913) **10** and **11**.

The ultimate strength of the wire tested at ordinary temperature was 65,000 lb. per sq. in. (4569 kg. per sq. cm.); elongation in 2 in. (5 cm.), 28 per cent.; diameter of wire, 0.073 in. (1.9 mm.).

The stress necessary to produce fracture in the hot wire is very small compared with the ultimate strength of the material at ordinary temperatures (approximately 5 per cent.). The appearance of the fracture is very characteristic, a sharp crystalline break with no appreciable elongation or reduction of cross-sectional area. A series of small transverse cracks, parallel and close to the face of the break, is usually to be found. Fig. 19 shows the appearance of two of the wires broken in this manner and shows the characteristic features of the fracture.

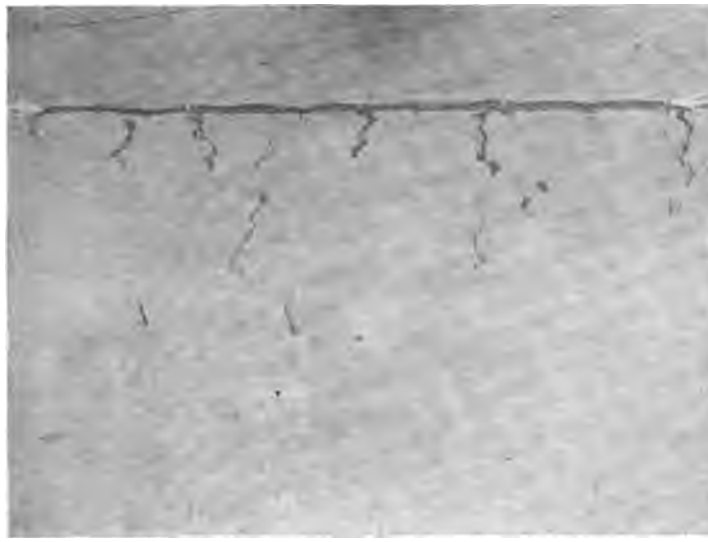
The changes in the microstructure produced by the combined action of

FIG. 19.—FRACTURED ENDS OF TWO NICKEL WIRES BROKEN IN TENSION WHILE HOT. × 5.

tensional stress and heat are shown in Fig. 20. A network of fine intercrystalline fissures with numerous transverse cracks extending into the body of the wire is produced. In Fig. 21 there is shown a section through the end of one of the fractured wires. The fracture is distinctly intercrystalline and has resulted from the formation of transverse intercrystalline cracks, which are identical in appearance with those found in the terminals that deteriorated in service.

The brittleness of metals at high temperatures has been explained by Rosenhain and Ewen[6] as due to the weakening of the intercrystalline "amorphous cement" upon heating. The behavior of nickel is very similar to that of lead, tin, and the other metals of relatively low melting point, which were used in the work of Rosenhain referred to. Nickel differs, however, in one important respect, in that the intercrystalline weakness becomes manifest at temperatures far below the melting point. Metals, such as tin, lead, and aluminum, must be heated to

[6] *Loc. cit.*



a. Unetched.

b. Etched 3 sec. with concentrated nitric acid. × 100.

FIG. 20.—LONGITUDINAL SECTION OF NICKEL WIRE STRESSED IN TENSION WHILE HOT UNTIL FRACTURE OCCURRED. ARROWS INDICATE EDGE OF SECTION.

within a few degrees of the melting point in order to demonstrate this intercrystalline weakness. Nickel also differs markedly from iron in its behavior at high temperatures. Rosenhain and Humfrey[7] demonstrated that iron and mild steel will break under a relatively very low stress at high temperatures with an intercrystalline break but with a very pro-

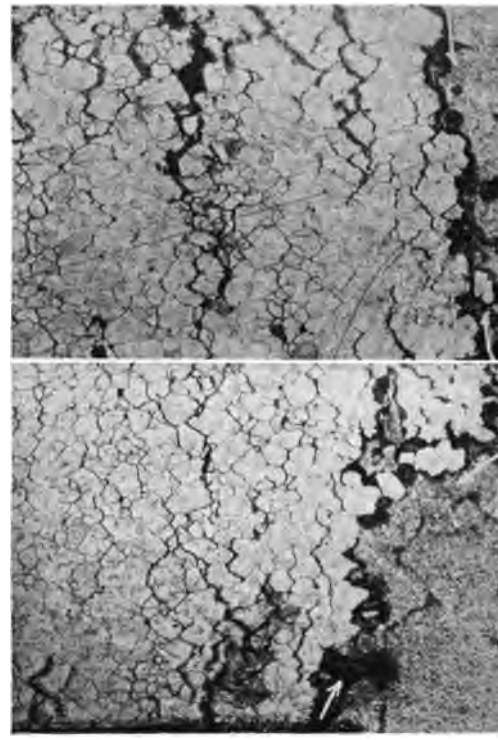


FIG. 21.—LONGITUDINAL SECTION THROUGH FRACTURE PRODUCED IN HOT WIRE UNDER CONSTANT LOAD; FRACTURE IS DISTINCTLY INTERCRYSTALLINE AND IDENTICAL IN APPEARANCE TO THOSE PRODUCED IN SERVICE. ARROWS INDICATE FACE OF FRACTURE. PHOTOMICROGRAPH SHOWS ENTIRE SECTION OF WIRE. ETCHING, CONCENTRATED NITRIC ACID FOR 3 SEC. × 65.

nounced elongation, often over 100 per cent. Nickel breaks with no elongation.

EXPLANATION OF SERVICE DETERIORATION OF TERMINALS

The types of deterioration of the nickel wires in service as spark-plug terminals are to be attributed to the combined effect of several causes. The surface layer of wires heated continuously in a reducing atmosphere shows evidence of intercrystalline brittleness. This be-

[7] W. Rosenhain and J. C. W. Humfrey: National Physical Lab., *Collected Researches*, **11**.

havior of nickel is in agreement with the fact that deterioration in service begins at the surface and progresses inward. Prolonged heating in the air will likewise develop brittleness in the outer layer by the formation of an intercrystalline eutectic-like network. This effect is very slight, however, in comparison with other causes and probably does not materially affect the rate of deterioration of the terminals. The increased crystal size due to prolonged heating will contribute somewhat to the failure of the wires by facilitating the formation of the transverse intercrystalline fissures.

Local overheating by the electric spark, with the subsequent cooling, gives rise to the definite intercrystalline fissures in such overheated areas that contribute to the local brittleness of the wire. The more rapid wearing away of the metal on the side exposed to the spark is probably due to this. The weakening of the "intercrystalline cement" upon heating and the pronounced intergranular separation that occurs upon application of a very low stress is probably, however, responsible for the definite "knife-cut" fractures that occur in some terminals. Such stresses may be due to the effect of unequal heating and cooling of the wire, to the vibratory and explosive action of the spark, and to the constant jarring and vibration of the engine as a whole in service; this is particularly pronounced in the case of airplane motors. The stressing of the side terminals firmly anchored at both ends by the differential expansion of the shell of the plug is probably, however, the most potent source of danger to which such terminals are exposed. The other possible stresses cited affect all terminals and probably aid materially in the formation of the intercrystalline network that is always formed and by which the wire is embrittled.

Summary

1. The service deterioration of nickel spark-plug terminals is shown to be due to the embrittlement of the wire by the formation of a system of intercrystalline network and definite transverse cracks.

2. Variations in chemical composition of the nickel wires do not appear to have much bearing on the deterioration; it occurs in wire of relatively high purity as well as in the "97-per cent. grade" usually specified.

3. Continued heating of nickel wire in the air at a high temperature contributes slightly to the embrittlement of the wire by the formation of an intercrystalline eutectic-like oxide network.

4. Nickel wires heated in a strongly reducing atmosphere show evidence of an intercrystalline embrittlement of the surface metal. A thin brittle surface skin, apparently carbide, forms in case considerable carbon is deposited on the wire.

5. Intense local heating by means of the electric spark together with

the sudden cooling contributes to the embrittling of the wire by the formation of fine intercrystalline fissures in the heated zone.

6. The application of a relatively low stress to the hot wire is sufficient to fracture the wire by the formation of transverse intercrystalline cracks. The tensional stress due to the differential expansion of the shell and the terminals is probably sufficient to cause the formation of the transverse breaks in those electrodes that are firmly anchored at both ends. Such cracks were not found in other forms of nickel terminals.

DISCUSSION

FRANCIS B. SILSBEE,* Washington, D. C. (written discussion).—This paper is an interesting example of the solution by the methods of metallography of what seemed at first a purely chemical problem. The authors have shown, in detail, how the well-known corrosion of spark-plug terminals is due to the dropping out of the individual crystals of the metal as it becomes surrounded by an oxide film. This corrosion is usually quite slow but in special cases may become a serious factor in limiting the life of spark plugs. There still remains the problem for the metallurgist to produce a material that will be entirely free from this trouble.

One of the most startling results of the work is the demonstration that it affords of the deleterious effect of a mechanical stress continuously applied to material that is at the same time subject to adverse chemical or thermal conditions. The particular style of spark plug shown in the illustration, and in which serious trouble was caused by this corrosion, has the side terminals fastened at both ends and the method of assembling is such that a considerable initial tension is applied to the wire. It is without doubt this superimposed tension that causes the intercrystalline network to line up, as it were, into a few continuous and deeply penetrating transverse fissures instead of forming a great number of shallow surface cracks. This result is clearly shown both in the case of wires suspended in the electric furnace and in the spark-plug terminals themselves.

This phenomenon is closely analogous in some respect to another case of deterioration, which, oddly enough, also arose in connection with the work that the Bureau of Standards has been carrying on during the past two years on spark plugs and ignition apparatus. The second instance is the cracking of the rubber insulation on the high-tension cables connecting the spark plugs to the distributor. The ozone produced by electrical discharges in the neighborhood of such cables attacks unstressed rubber uniformly and very slowly. The presence of a very little mechanical tension in the insulation, however, is sufficient to localize the corrosion

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into a few deep cracks, which rapidly extend to the core of the cable and render it useless. This failure of the cable and the breaking of the nickel wire described in this paper are doubtless only two of the many similar cases where a material fails under a combination of adverse conditions, no one of which is alone sufficient to cause any serious damage.

PAUL D. MERICA, Bayonne, N. J. (written discussion).—The mode of intercrystalline oxidation which the authors have so well observed and described is characteristic of nickel that has been exposed to the action of an oxidizing atmosphere at higher temperatures, such as those at

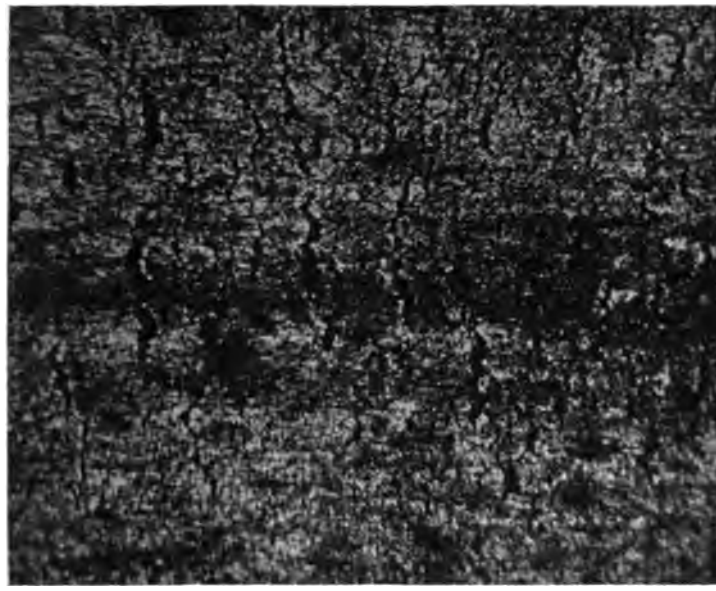


FIG. 22.—UNETCHED SURFACE OF SAME NICKEL SHEET SHOWING SURFACE CRACKING AND CHECKING DUE TO OXIDATION. × 100.

which it is annealed or heated for rolling or forging. Oxidation under such conditions proceeds inward from the surface along the crystal boundaries producing a network, probably of oxide, which causes a very brittle condition of this surface material. This, in turn, generally results in surface cracking and checking during further rolling and a defective sheet or other product is produced.

An example of this is shown in Fig. 22, which shows the surface of a badly surface-cracked sheet of nickel produced by incorrect heating conditions. A cross-section of this sheet etched with nitric acid is shown in Fig. 23, which reveals the intercrystalline oxidation network adjacent to

both surfaces. These layers are so brittle that it is not possible to deform them by rolling without severe cracking along these lines or planes of weakness. The best, and possibly only, remedy for this condition lies in its prevention by the maintenance of a neutral soft flame for heating and annealing nickel during the entire course of its manufacture.

I should like to suggest that those making microscopic investigations of nickel and nickel-rich alloys try the use of acetic-acid solutions of nitric acid for etching these metals rather than aqueous solutions of nitric

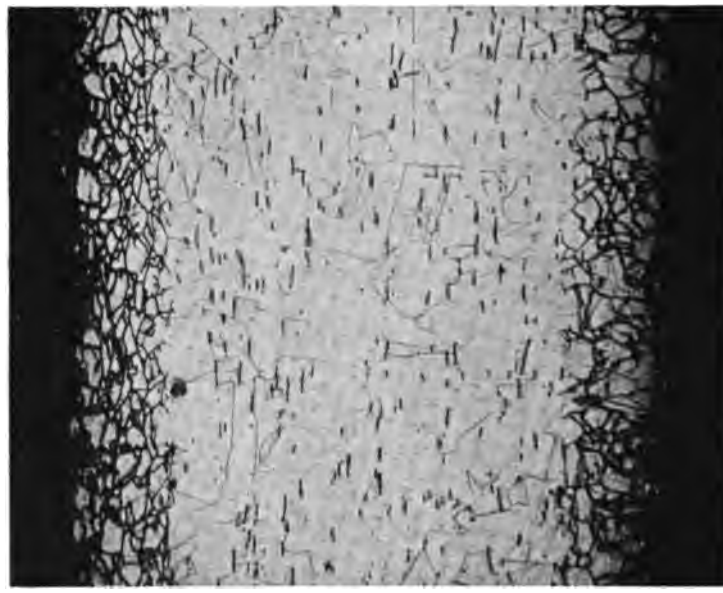


FIG. 23.—CROSS-SECTION OF NICKEL SHEET ETCHED WITH NITRIC ACID (50 PER CENT. IN 50 PER CENT. ACETIC ACID) SHOWING INTERCRYSTALLINE OXIDATION OF SURFACE LAYERS. × 100.

acid. I have found that a solution containing 50 per cent. nitric acid, from 25–45 per cent. acetic acid, and from 25–5 per cent. water gives excellent results with wrought and cast nickel and Monel metal and superior results to those obtained with nitric acid alone. The acetic acid seems to inhibit the passivity that nickel often assumes toward nitric acid and much more uniform etching may be obtained. The proportions of nitric and acetic acid may be varied somewhat from those given without materially altering the quality of the etching, although without any distinct improvement in it.

Grain Growth in Alpha Brass

BY F. G. SMITH,* S. B., WATERBURY, CONN.

(Philadelphia Meeting, September, 1919)

A FEW years ago, the writer encountered a problem that, at first, seemed to be due to peculiar conditions affecting grain growth. Large cups made from heavy metal failed in the first drawing operation in the process of making seamless tubes. The metal, as cast, appeared to be sound and strong; it rolled successfully and withstood the first cupping operation, but on the first draw it failed, with a crystalline fracture. The failure appeared in the slightly worked part of the bottom of the cup, and microscopic examination revealed exceptionally large grains.

Knowing the general conditions governing recrystallization of brass, which were later published by Mathewson and Phillips,[1] an investigation was outlined with the idea of including various conditions under which new grains might form, and which would include the effect that a previous anneal might have upon the anneal following. These conditions were produced by annealing specimens of brass at five different temperatures, indenting them with a 10-mm. ball under four different pressures, and then reannealing at each of the five temperatures five specimens each of which had been annealed at one of the five temperatures.

PREPARATION OF SPECIMENS

The material used was cartridge brass 0.400 in. thick, having the following composition: Copper 66.60 per cent., zinc 33.35 per cent., lead 0.02 per cent., iron 0.03 per cent. This was rolled with 35 per cent. reduction after a 700° C. anneal. Fig. 1 shows the structure of this original bar on which all subsequent anneals were made. Pieces 1 in. (2.5 cm.) wide and 3 in. long were prepared and annealed for ½ hr. at 450°, 550°, 650°, 750°, and 850° C. Each of these pieces are indented under the Brinell test with a 10-mm. ball at 500, 1000, 2000, and 3000 kg. pressure. Then, sets of five pieces from each of the original anneals were reannealed at 450°, 550°, 650°, 750°, and 850° C.

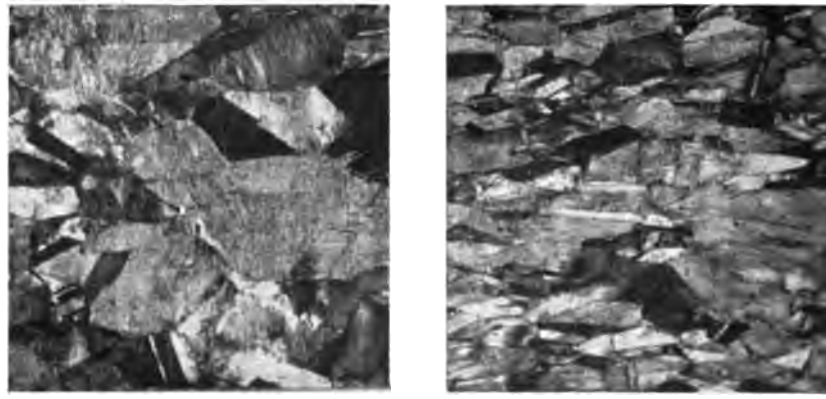
* Metallurgist, American Brass Co.

[1] *Trans.* (1916) **54**, 608.

Description of Structure as Shown by Macrographs

Fig. 2 shows the progressive grain size due to the anneals and, to some extent, the deformation under the ball impressions. Fig. 9 shows the structure of these anneals at 75 diameters.

Fig. 3 shows the five anneals after reannealing ½ hr. at 450° C. This series, when compared with Fig. 2, shows recrystallization under the ball impressions. Examination under the microscope shows a decrease in the amount of recrystallization with decrease in deformation on each specimen. A decrease in the amount of recrystallization with increase of previous anneal under a ball deformation made by a constant load does not take place. The explanation is that the same load does



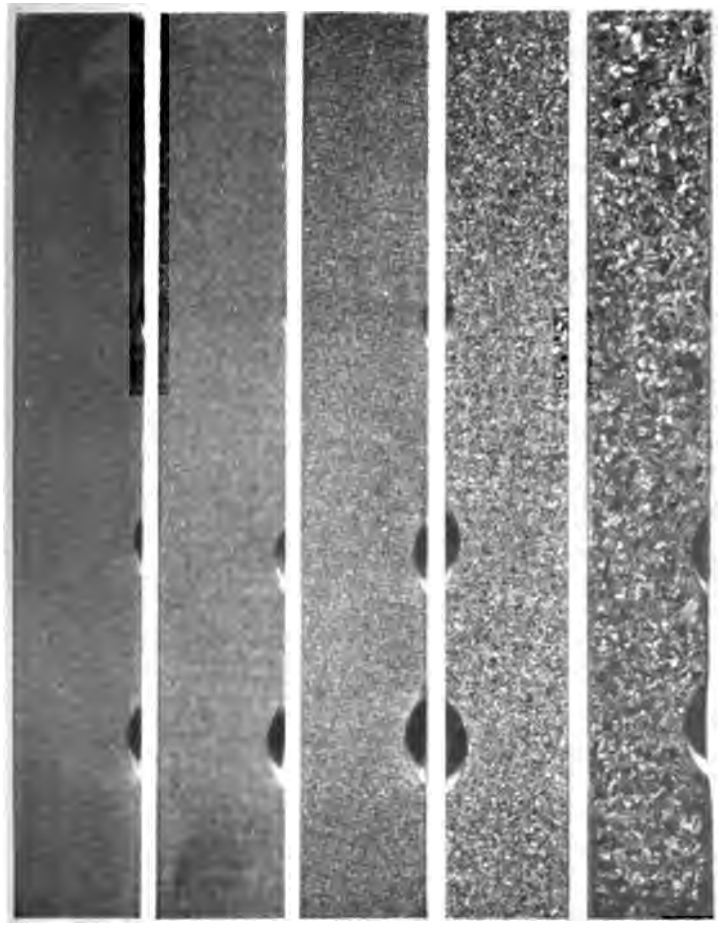
a. Longitudinal section parallel to surface. *b*. Longitudinal section perpendicular to surface.

Fig. 1.—Thirty-five per cent. reduction after 700° C. anneal. Etched with ammonia and hydrogen peroxide. × 75.

not produce the same deformation after a light anneal that it does after a heavy anneal. Also, a certain load may produce local severe deformation on the light annealed metal and a general and slight deformation on the heavily annealed metal. The crystalline equilibrium overbalances the effects in the higher anneals. It will be observed that under the deepest impression (3000 kg.) the amount of recrystallization increases with the amount of deformation up to 650° original anneal, but decreases to almost nothing beyond, due to the more stable equilibrium. The unworked portions of all pieces originally annealed above 450° C. were not recrystallized. There are no apparent zones of abnormal grains. Figs. 10, 11, and 12 show, at 75 diam., changes in structure under above conditions.

Fig. 4 shows the five anneals after reannealing ½ hr. at 550° C. This series, compared with Fig. 2, shows an increase in the amount of recrystallization under the ball impression, complete recrystallization in the specimen originally annealed at 450° C., but no recrystallization in

the unworked portions of specimens originally annealed above 550° C. There are zones of abnormal grains in the specimens originally annealed at 450° and 550° C. but none in specimens originally annealed above 550° C.



a. ½ hr. 450° C. *b*. ½ hr. 550° C. *c*. ½ hr. 650° C. *d*. ½ hr. 750° C. *e*. ½ hr. 850° C.

FIG. 2.—FIVE ORIGINAL ANNEALS. × 1⅔.

It will be shown in the accompanying plates that the ideal condition for the growth of abnormal grains in this series is attained in the specimen reannealed at 550° C. The abnormal grains in the specimen reannealed at 450° C. are the result of its being heated slowly through its germinative temperature (450° C.). Figs. 13, 14, 15 show, at 75 diam., the structure under these conditions.

Fig. 5 shows the five anneals after reannealing ½ hr. at 650° C. This series, compared with Fig. 2, shows a slight increase in the amount of recrystallization under the ball impressions in the softer specimens, complete recrystallization in the unworked portions of specimens originally annealed at 450° and 550° for ½ hr., but no recrystallization in

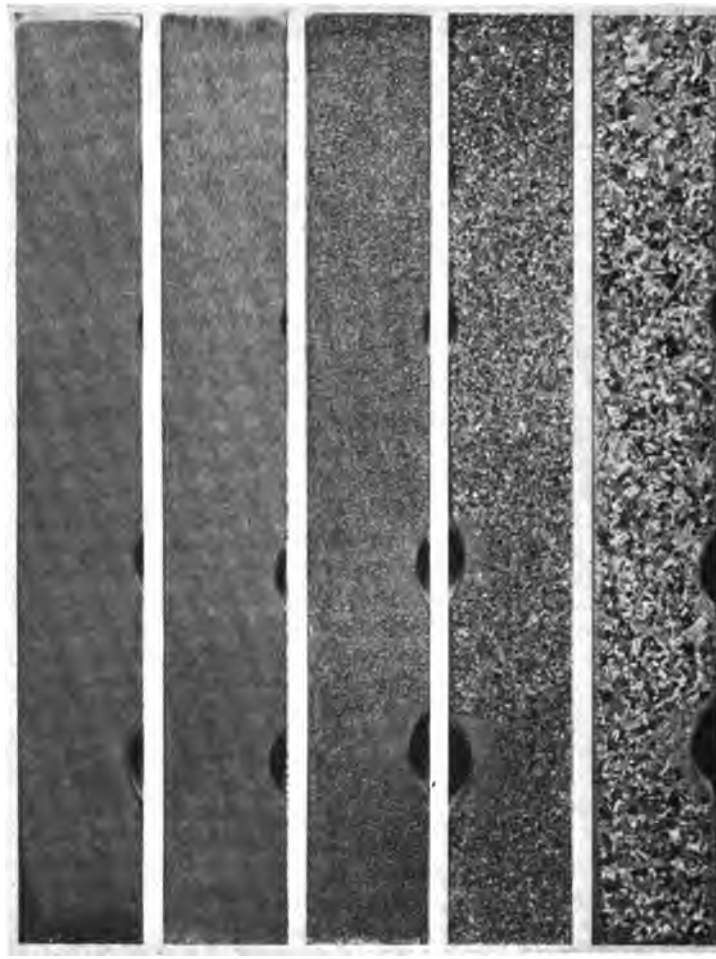


FIG. 3.—FIVE ORIGINAL ANNEALS AFTER REANNEALING ½ HR. AT 450° C. × 1⅜.

the unworked portions of specimens originally annealed above 650° C. There are distinct zones of abnormal grains in specimens originally annealed at 650° C., none in specimens originally annealed above 650° C., and only a few in specimens originally annealed below 650° C. No abnormal grains are found in specimens originally annealed above 650° C. because the germinative temperature of the whole specimen has not been reached, and normal recrystallization only has taken place. The few

abnormal grains in the specimen originally annealed below 650° C. are the remains of those formed while the specimens were being heated through their germinative temperatures, 450° and 550° C. The distinct zones of abnormal grains in the specimen originally annealed at 650° C. are due to the fact that the germinative temperature of the unworked

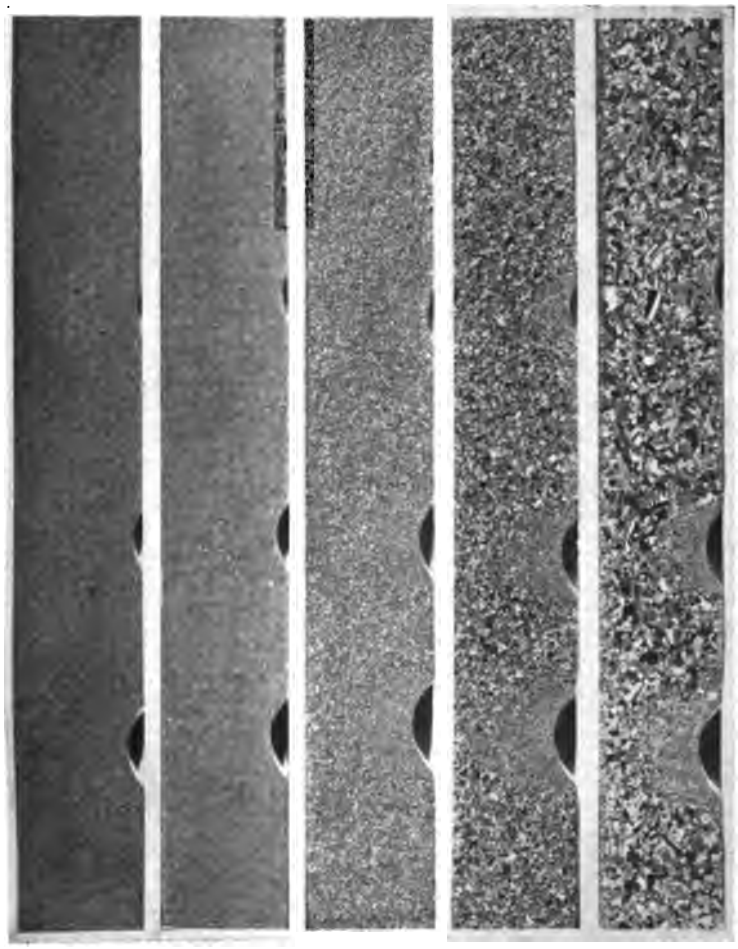
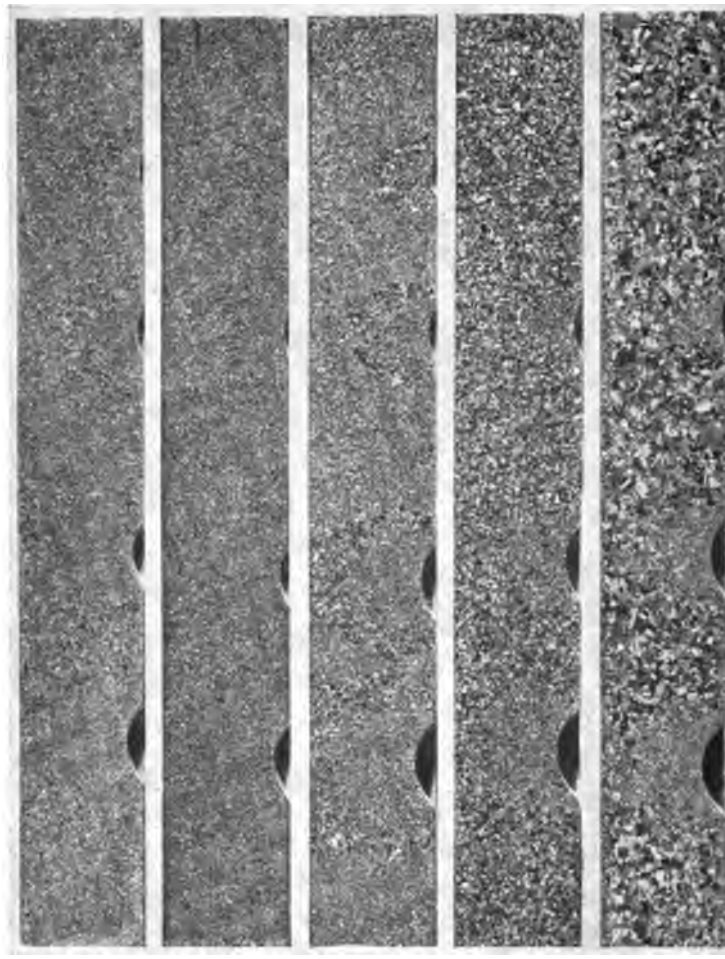


FIG. 4 —FIVE ORIGINAL ANNEALS AFTER REANNEALING ½ HR. AT 550° C. × 1⅔.

portions was identical with the temperature of the final anneal which caused recrystallization under the ball impressions. Figs. 16, 17, 18 show, at 75 diam., the structure under these conditions.

Fig. 6 shows the five anneals after reannealing ½ hr. at 750° C. This series, compared with Fig. 2, shows a further increase in the amount of recrystallization under the ball impressions, complete re-

crystallization in the unworked portions of specimens originally annealed below 750° C., but no recrystallization in the unworked portions of specimen annealed above 750° C. There are distinct zones of abnormal grains in the specimen originally annealed at 750° C.; but none in other specimens. The germinative temperature of the specimens originally



a *b* *c* *d* *e*

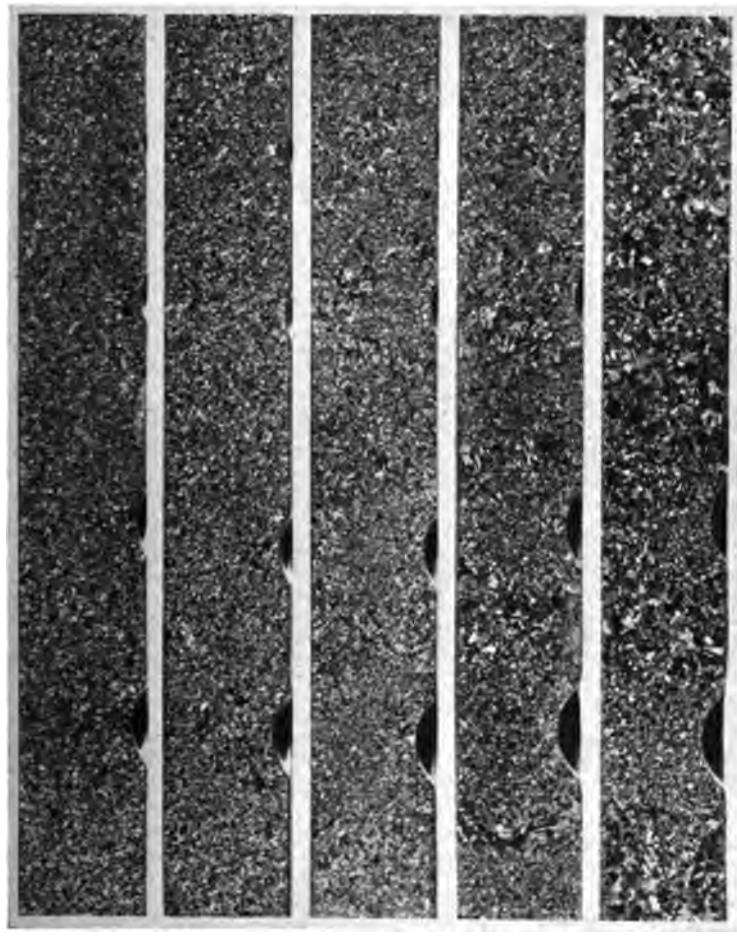
FIG. 5.—FIVE ORIGINAL ANNEALS AFTER REANNEALING ½ HR. AT 650° C. × 1⅓.

annealed below 750° C. were so much exceeded, or specimens were heated so quickly through this range that only a few grains were formed. Figs. 19, 20, 21 show, at 75 diam., the structure under these conditions.

Fig. 7 shows the five anneals after reannealing ½ hr. at 850° C. This series shows complete recrystallization of all specimens originally annealed below 850° C. and a few large grains in specimen annealed at

850° C. There are no well-defined zones, however, because the ball impressions were too near together and the specimen was not thick enough to allow the zones to form. Figs. 22, 23 show, at 75 diam., the structure under these conditions.

Fig. 8 illustrates the effect of prolonging the time of anneal on recrystallization and growth of abnormal grains. *a* and *b* were originally



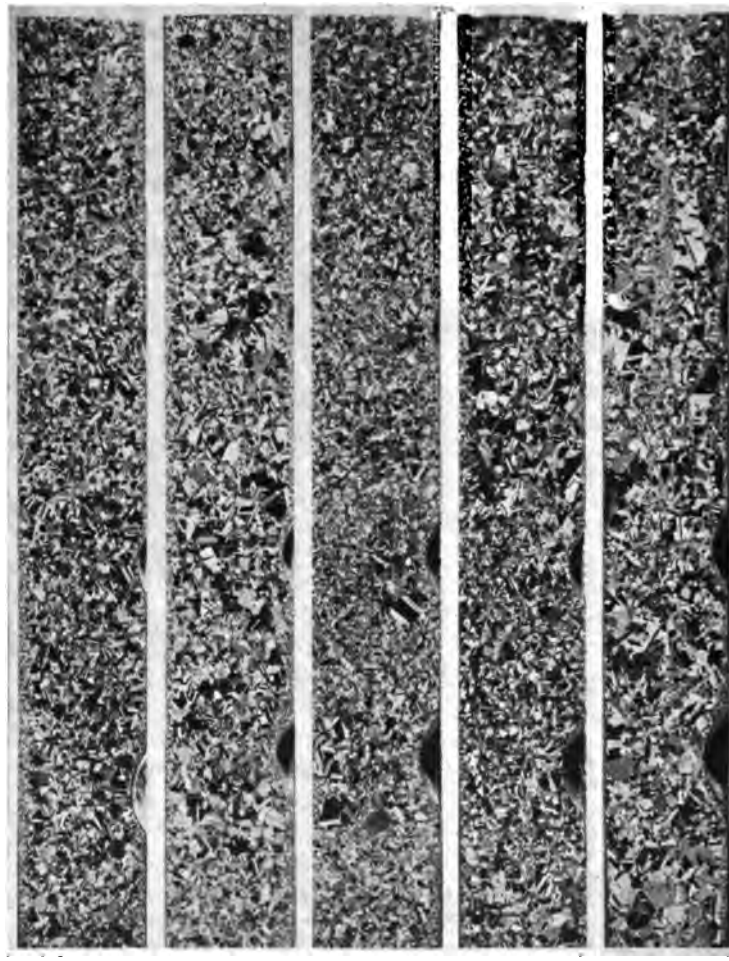
a *b* *c* *d* *e*

FIG. 6.—FIVE ORIGINAL ANNEALS AFTER REANNEALING ½ HR. AT 750° C. × 1⅜.

annealed ½ hr. at 550° C. *a* was reannealed for ½ hr. at 550° C. and *b* reannealed for 5 hr. at 550° C. *c* and *d* were originally annealed ½ hr. at 650° C., *c* was reannealed for ½ hr. at 650° C., and *d* reannealed for 5 hr. at 650° C.

It was shown, in the previous figures, that reannealing at the original temperature and time did not affect the unworked portions. In the

case of the 5-hr. reanneals at the original temperature the unworked portions have recrystallized. The zones of abnormal grains cover a larger area, and the abnormal grains have increased in size. The structure at 75 diameters under these conditions is shown at *b* and *c*, Figs. 13, 14, and 15, and at *c* and *d*, Figs. 16, 17, 18.



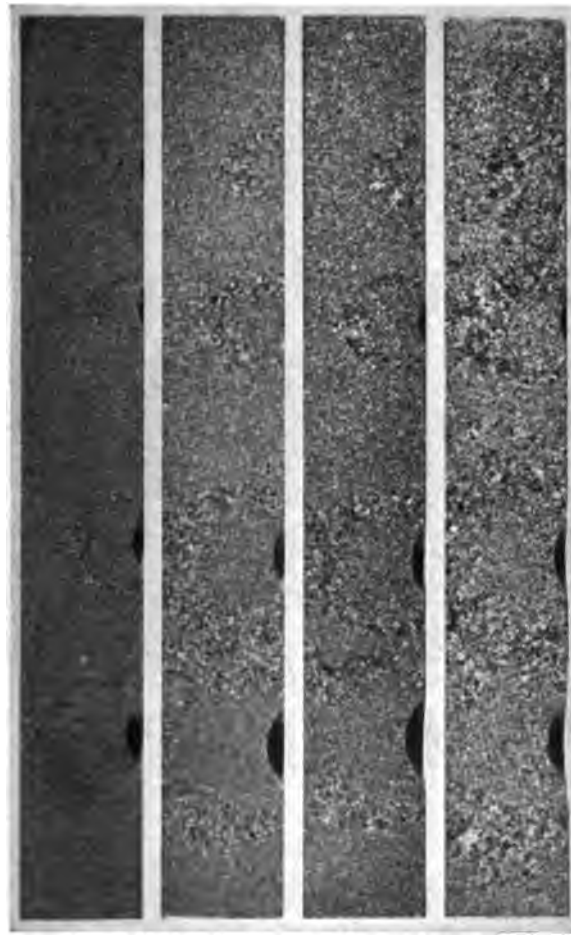
a *b* *c* *d* *e*

FIG. 7.—FIVE ORIGINAL ANNEALS AFTER REANNEALING ½ HR. AT 850° C. × 1⅜

DESCRIPTION OF STRUCTURE AS SHOWN BY MICROGRAPHS

Original Anneal.—Fig. 9 shows the structure of the original anneals at 75 diameters. At *e* is shown a part of a very large grain, which will be referred to later.

After Reannealing at 450° *C.*—Fig. 10 shows the structure under 3000 kg. impression after reannealing the five original pieces at 450° C. for ½ hr. It illustrates how the previous anneal affects the grain size on recrystallization after deformation. The grain is refined in every case, but germinant grains are larger with increase of original anneal until, at *e*,



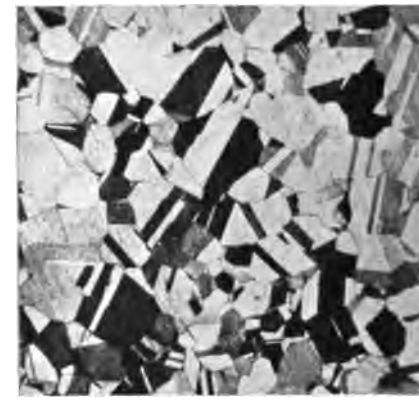
a. ½ hr. 550° C. *b.* 5 hr. 550° C. *c.* ½ hr. 650° C. *d.* 5 hr. 650° C.

FIG. 8.—EFFECT OF PROLONGING TIME OF REANNEAL AT 550° C. AND 650° C. × 1⅞.

the point is reached where only parts of the original grains are recrystallized. Particular attention is called to the location of these new grains, which have begun to form either at the grain boundaries or along the boundaries of twin bands. A careful examination did not reveal any new grains forming along slip bands within the crystal boundaries,

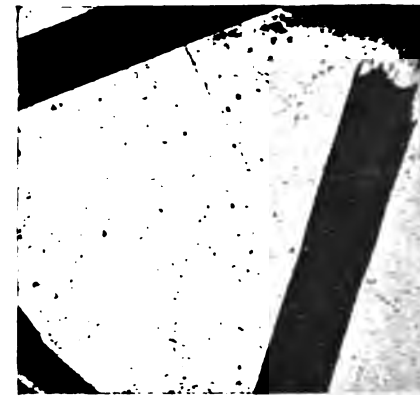
a. 450° C. for ½ hr.

b. 550° C. for ½ hr.



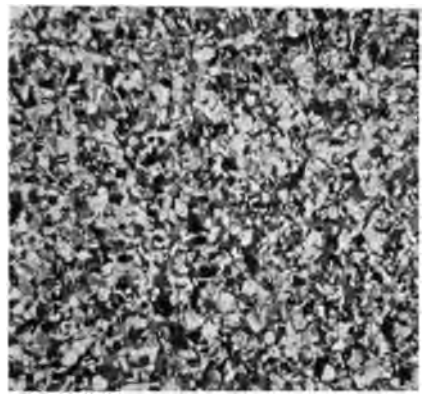
c. 650° C. for ½ hr.

d. 750° C. for ½ hr.

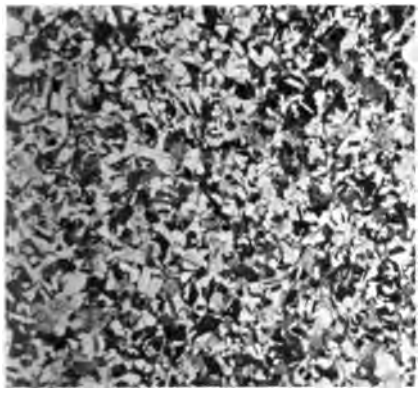


e. 850° C. for ½ hr.

FIG. 9.—ORIGINAL ANNEALS. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.



a. 450° C. for ½ hr. after 450° C. for ½ hr.



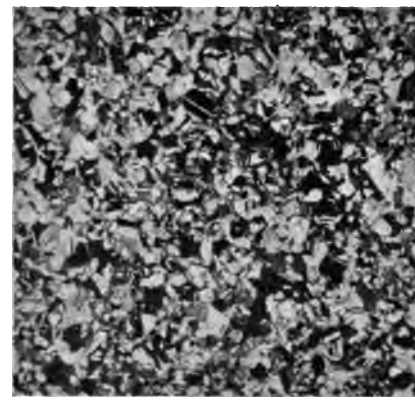
b. 450° C. for ½ hr. after 550° C. for ½ hr.

c. 450° C. for ½ hr. after 650° C. for ½ hr.

d. 450° C. for ½ hr. after 750° C. for ½ hr.

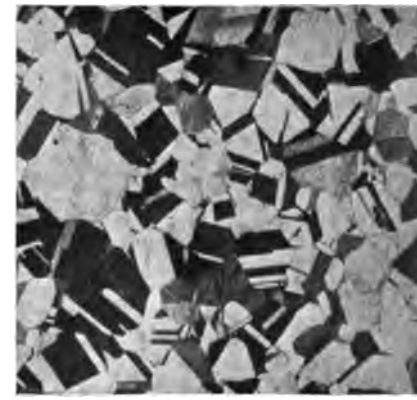
e. 450° C. for ½ hr. after 850° C. for ½ hr.

FIG. 10.—STRUCTURE UNDER 3000 KG. IMPRESSION, AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 450° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.



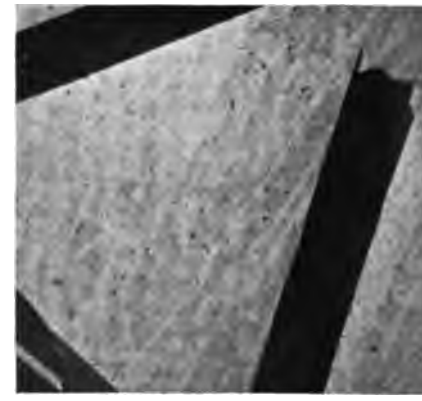
a. 450° C. for ½ hr. after 450° C. for ½ hr.

b. 450° C. for ½ hr. after 550° C. for ½ hr.



c. 450° C. for ½ hr. after 650° C. for ½ hr.

d. 450° C. for ½ hr. after 750° C. for ½ hr.

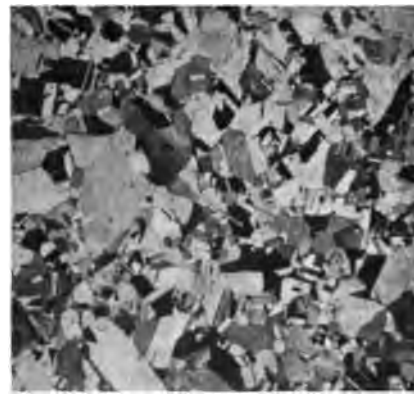


e. 450° C. for ½ hr. after 850° C. for ½ hr.

FIG. 11.—STRUCTURE OF FIVE ORIGINAL PIECES REANNEALED AT 450° C. WITHOUT INTERMEDIATE DEFORMATION. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 450° C. for ½ hr. after 450° C. for ½ hr.

b. 450° C. for ½ hr. after 550° C. for ½ hr.



c. 450° C. for ½ hr. after 750° C. for ½ hr.

FIG. 12.—STRUCTURE IN GERMINATIVE AREAS AFTER REANNEALING AT 450° C.; THE ORIGINAL PIECES ANNEALED AT 450° C., 550° C. AND 750° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

Mathewson and Phillips have suggested that deformation in metals is a process of grain fragmentation and recrystallization a coalescence of these grain fragments. I should prefer to explain these phenomena by Beilby's amorphous theory, which postulates that there is always amorphous material at grain boundaries and that amorphous material is formed within the grains by deformation. It follows that there should always be more amorphous material at grain boundaries after any deformation and that with subsequent annealing new grains should always form first at the grain boundaries.

Fig. 11 shows the structure in specimens reannealed at 450° C. in areas not affected by deformation. A comparison with Fig. 9 shows that the grains have not grown. At *e* is the identical crystal shown in Fig. 9; there has been no recrystallization.

Fig. 12 shows the structure at 75 diameters in the germinative areas of three specimens reannealed at 450° C. At *a* is shown the abnormal grains produced under these conditions, which should be compared with *a*, Fig. 10. At *b* is shown a few slightly enlarged grains, which should be compared with *b*, Figs. 9 and 10. At *c* is shown normal recrystallization under these conditions. The larger grains are parts of crystals remaining from the old crystallization. It should be compared with *d*, Fig. 10.

Structure After Reannealing at 550° *C.*—Fig. 13 shows the structure under 3000 kg. impression after reannealing the five original specimens at 550° C. There is complete recrystallization in each case and only a slight change in grain size due to previous anneal in those specimens reannealed for ½ hr. This figure should be compared with Fig. 10. At *c* is shown the structure after annealing for 5 hr. at 550° C.; at this annealing temperature, time has considerable influence on grain size.

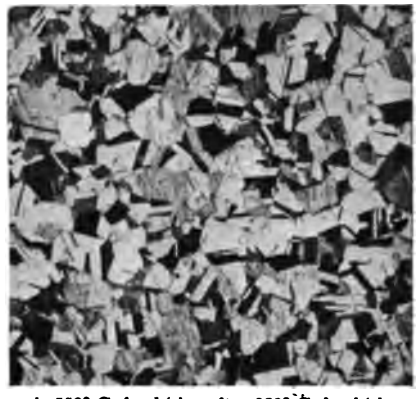
Fig. 14 shows the structure of specimens reannealed at 550° C. in areas not affected by deformation. A comparison with Fig. 9 shows that the reanneal for ½ hr. has no effect on crystal growth when the final anneal was below or at the temperature of the original anneal. The specimen *a*, originally annealed at 450° C. for ½ hr. and again at 550° for ½ hr., has a grain size normal for the final anneal. It should be compared with *b*, Fig. 9. At *c* is shown the structure after reannealing for 5 hr. at 550° C.

Fig. 15 shows the structure in the germinative zones after reannealing specimens at 550° C. At *a* and *b* are shown slightly enlarged grains in the germinative zones; see *b*, Fig. 9, and *a*, Fig. 14, for a comparison of grain sizes. At *c* is shown the structure in the germinative zone after reannealing for 5 hr. at 550° C. See also *b*, Fig. 9. The photograph plainly shows the characteristics of abnormal grains; they are always banded with twin crystals in a regular manner. In these specimens the bands were always either at 90° or 60° angles. At *d* is shown only a slight trace of abnormal grains, and *e* and *f* have nearly a normal structure.

a. 550° C. for ½ hr. after 450° C. for ½ hr.

b. 550° C. for ½ hr. after 550° C. for ½ hr.

c. 550° C. for 5 hr. after 550° C. for ½ hr.



d. 550° C. for ½ hr. after 650° C. for ½ hr.

e. 550° C. for ½ hr. after 750° C. for ½ hr.

f. 550° C. for ½ hr. after 850° C. for ½ hr.

FIG. 13.—STRUCTURE UNDER 3000 KG. IMPRESSION FATER REANNEALING THE FIVE ORIGINAL PIECES AT 550° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 550° C. for ½ hr. after 450° C. for ½ hr.

b. 550° C. for ½ hr. after 550° C. for ½ hr.

c. 550° C. for 5 hr. after 550° C. for ½ hr.

d. 550° C. for ½ hr. after 650° C. for ½ hr.

e. 550° C. for ½ hr. after 750° C. for ½ hr.

f. 550° C. for ½ hr. after 850° C. for ½ hr.

FIG. 14.—STRUCTURE OF FIVE ORIGINAL PIECES REANNEALED AT 550° C. WITHOUT INTERMEDIATE DEFORMATION. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 550° C. for ½ hr. after 450° C. for ½ hr.

b. 550° C. for ½ hr. after 550° C. for ½ hr.

c. 550° C. for 5 hr. after 550° C. for ½ hr.

d. 550° C. for ½ hr. after 650° C. for ½ hr.

e. 550° C. for ½ hr. after 750° C. for ½ hr.

f. 550° C. for ½ hr. after 850° C. for ½ hr.

FIG. 15.—STRUCTURE IN GERMINATIVE ZONES AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 550° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 650° C. for ½ hr. after 450° C. for ½ hr.

b. 650° C. for ½ hr. after 550° C. for ½ hr.

c. 650° C. for ½ hr. after 650° C. for ½ hr.

d. 650° C. for 5 hr. after 650° C. for ½ hr.

e. 650° C. for ½ hr. after 750° C. for ½ hr.

f. 650° C. for ½ hr. after 850° C. for ½ hr.

FIG. 16.—STRUCTURE UNDER 3000 KG. IMPRESSION AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 650° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 650° C. for ½ hr. after 450° C. for ½ hr.

b. 650° C. for ½ hr. after 550° C. for ½ hr.

c. 650° C. for ½ hr. after 650° C. for ½ hr.

d. 650° C. for 5 hr. after 650° C. for ½ hr.

e. 650° C. for ½ hr. after 750° C. for ½ hr.

f. 650° C. for ½ hr. after 850° C. for ½ hr.

FIG. 17.—STRUCTURE OF FIVE ORIGINAL PIECES REANNEALED AT 650° C. WITHOUT INTERMEDIATE DEFORMATION. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

Structure After Reannealing at 650° *C.*—Fig. 16 shows the structure under 3000 kg. impression after reannealing the five original pieces at 650° C. Each specimen is completely recrystallized and there is the uniform grain size characteristic of the 650° C. anneal, regardless of the previous annealing temperature. Compare *a*, *b*, *c*, *e*, and *f* with *c*, Fig. 9. At *d* is shown the structure after reannealing for 5 hr. at 650° C.; at this annealing temperature time has very little influence on grain size.

Fig. 17 shows the structure of specimens reannealed at 650° C. in areas not affected by deformation. *a* and *b* show that the grains of the original anneal have been replaced by new grains, which are normal for the final anneal at 650° C. Compare with *c*, Fig. 9. *d* shows no change in grain size after reannealing for 5 hr. at 650° C. *e* and *f* show that specimens originally annealed at 750° and 850° C. were not affected by the reanneal at 650° for ½ hr.

Fig. 18 shows the structure in the germinative zones after reannealing specimens at 650° C. *a* and *b* show a few remnants of abnormal grains in the specimens originally annealed at 450° and 550° C. which were formed while these specimens were being heated through their respective germinative temperatures. *c* and *d* show the characteristic abnormal grains. *d* after reannealing for 5 hr. at 650° C. shows portions of very large grains. *e* and *f* show a structure more nearly normal, although they have some characteristics of abnormal grains. These grains were at the border of the recrystallized zones shown at *d*, Fig. 5, and are no doubt a mixture of the old and new crystallization rather than new abnormal grains.

After Reannealing at 750° *C.*—Fig. 19 shows the structure under 3000 kg. impression after annealing the five specimens at 750° C.; each specimen was completely reannealed and has a uniform grain size. However, the grains were larger than in the specimen originally annealed at 750°. This figure should be compared with *d*, Fig. 9, and *a*, *b*, and *c*, Fig. 6.

Fig. 20 shows the structure of specimens reannealed at 750° C. in areas not affected by deformation. *a*, *b*, and *c* show that grains of the original anneals below 750° C. have been replaced by new grains, which are normal for the final anneal at 750° C. Compare with *d*, Fig. 9; *d* and *e*, Fig. 20, show no change in grain size.

Fig. 21 shows the structure in the germinative zones after reannealing specimens at 750° C. *a* shows no abnormal grains; compare with *d*, Fig. 9, and *a*, Fig. 17. This specimen was probably heated through its germinative temperature (450° C.) so rapidly that no grains were formed which were larger than those formed at the maximum temperature. *b* and *c* show few abnormal grains; there are more in *c* than in *b*; see *b* and *c*, Fig. 7. *d* shows about one-fifth of a large abnormal grain and *e* shows a few grains in the area of recrystallization that have some characteristics of abnormal grains.

a. 650° C. for ½ hr. after 450° C. for ½ hr.

b. 650° C. for ½ hr. after 550° C. for ½ hr.

c. 650° C. for ½ hr. after 650° C. for ½ hr.

d. 650° C. for 5 hr. after 650° C. for ½ hr.

e. 650° C. for ½ hr. after 750° C. for ½ hr.

f. 650° C. for ½ hr. after 850° C. for ½ hr.

FIG. 18.—STRUCTURE IN GERMINATIVE ZONES AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 650° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 750° C. for ½ hr. after 450° C. for ½ hr.

b. 750° C. for ½ hr. after 550° C. for ½ hr.

c. 750° C. for ½ hr. after 650° C. for ½ hr.

d. 750° C. for ½ hr. after 750° C. for ½ hr.

e. 750° C. for ½ hr. after 850° C. for ½ hr.

FIG. 19.—STRUCTURE UNDER 3000 KG. IMPRESSION AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 750° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

a. 750° C. for ½ hr. after 450°C. for ½ hr.

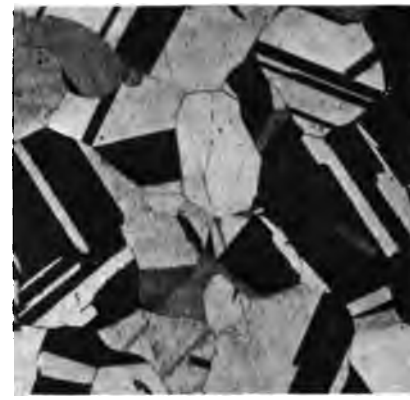
b. 750° C. for ½ hr. after 550° C. for ½ hr.

c. 750° C. for ½ hr. after 650° C. for ½ hr.

d. 750° C. for ½ hr. after 750° C. for ½ hr.

e. 750° C. for ½ hr. after 850° C. for ½ hr.

FIG. 20.—STRUCTURE OF FIVE ORIGINAL PIECES REANNEALED AT 750° C. WITHOUT INTERMEDIATE DEFORMATION. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.



a. 750° C. for ½ hr. after 450° C. for ½ hr.

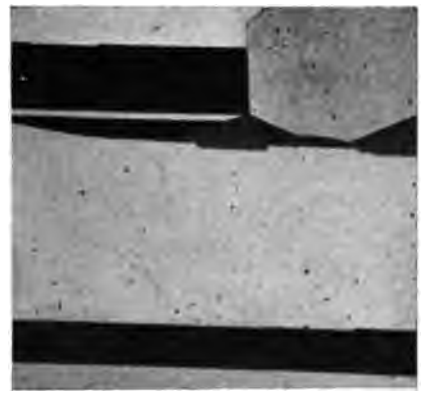
b. 750° C. for ½ hr. after 550° C. for ½ hr.

c. 750° C. for ½ hr. after 650° C. for ½ hr.

d. 750° C. for ½ hr. after 750° C. for ½ hr.

e. 750° C. for ½ hr. after 850° C. for ½ hr.

FIG. 21.—STRUCTURE IN GERMINATIVE ZONES AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 750° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.



a. 850° C. for ½ hr. after 450° C. for ½ hr.

b. 850° C. for ½ hr. after 550° C. for ½ hr.

c. 850° C. for ½ hr. after 650° C. for ½ hr.

d. 850° C. for ½ hr. after 750° C. for ½ hr.

e. 850° C. for ½ hr. after 850° C. for ½ hr.

FIG. 22.—STRUCTURE UNDER 3000 KG. IMPRESSION AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 850° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75

a. 850° C. for ½ hr. after 450° C. for ½ hr.

b. 850° C.for ½ hr. after 550° C. for ½ hr.

c. 850° C. for ½ hr. after 650° C. for ½ hr.

d. 850° C. for ½ hr. after 750° C. for ½ hr.

e. 850° C. for ½ hr. after 650° C. for ½ hr.

FIG. 23.—STRUCTURE IN GERMINATIVE AREAS AFTER REANNEALING THE FIVE ORIGINAL PIECES AT 850° C. ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE. × 75.

After Reannealing at 850° *C.*—Fig. 22 shows the structure under 3000 kg. impression after annealing the five specimens at 850° C. The grains are somewhat larger than the normal grains after an anneal at 850° C. Compare Fig. 8 with *e*, Fig. 2.

Fig. 23 shows the structure in germinative areas after annealing at 850° C. *a*, *b*, and *c* show a grain size about normal for the temperature of anneal; *d* and *e* show small parts of abnormal grains. The general size of these grains can be better appreciated by referring to *e*, Fig. 7. The largest grain found was about 6 mm. in its greatest diameter. No mention has been made of crystalline growth under the 500-, 1000-, 2000-kg. impressions for all the conditions and results were similar and differed only in degree.

Conclusions

There are four conclusions to be drawn from the foregoing study of crystalline growth after annealing, which supplement or confirm work that has been done by Mathewson and Phillips, Jeffries, and others on this subject. They are:

1. That brass which has received an anneal at a low temperature previous to a given deformation will recrystallize at a lower temperature and develop a finer grain than that which was originally annealed at a higher temperature; in other words, with a given deformation, the recrystallization temperature and resultant grain size vary directly with the temperature of anneal before deformation, Fig. 10.

2. That upon reannealing brass without intermediate deformation, there is no grain growth unless the time and temperature of the first anneal are exceeded in the second anneal, Figs. 3, 4, 5, 6, 14, 17 and 20.

3. That the length of time of anneal has a greater effect on resultant grain-size at low temperature than it has at high temperatures, Figs. 13 and 16.

4. That the ideal conditions under which typical abnormal grains are formed are that there shall be a deformation gradient, which ranges from a maximum to zero within the specimen, and the temperature of anneal before such deformation shall be identical with the final temperature of anneal. The size of the abnormal grains varies with the length of time of the last anneal. Results indicate that the time of the previous anneal may also affect the size of abnormal grains in that it establishes a more stable equilibrium which has to be overcome before the abnormal grains can develop.

This investigation was carried out before the papers by Mathewson and Phillips and by Zay Jeffries on recrystallization were published, and those papers have been extremely interesting in that they have served to explain the causes of the results here found. It is realized that the third conclusion arrived at is already well recognized and has been the subject

of discussion in many papers. At least one conclusion relative to formation of abnormal grains supplements the very extensive work done by Doctor Jeffries on this subject.

In his paper, "Grain Growth Phenomena in Metals,"[2] Zay Jeffries states that the "formation of large grains at the germinative temperature is dependent on a rather even grain size with temperature gradient, or even temperature with deformation gradient, or any combination of the two." The latter condition will not always produce abnormal grains. The specimen shown at *c*, Fig. 3, was annealed under such conditions but no large grains have formed because the final temperature, 450° C., was not high enough to recrystallize any but the hardest portions within the deformed area. The specimen shown at *c*, Fig. 5, which was annealed under the same conditions as the above, except that the final temperature was high enough to disturb the equilibrium of the unworked portions, shows distinct zones of abnormal grains. If it were possible, and it appears probable, that specimen *c*, Fig. 3, could have been annealed for sufficient time at 450° C. to cause a recrystallization in the unworked portions previously annealed at 650° C., abnormal grains would have formed but not under the most favorable circumstances.

The formation of these large grains is analogous to the formation of large crystals from a saturated salt solution. The unworked portions of metal represent the solution that is in equilibrium, and the local deformation represents the nucleus of crystal growth. Upon heating, crystallization soon begins at the nucleus and proceeds with the formation of a few fine grains until the recrystallization temperature of the unworked portions is reached. This unworked portion corresponds to saturation in a salt solution. At this point large crystals will form and the longer the temperature is held at the recrystallization point the larger will be the grains, just as crystals will continue to grow larger from a salt solution kept near its saturation point.

The adjective "abnormal" has been used to describe the large grains formed under certain conditions because they are abnormal when compared with those obtained from ordinary practice, but in reality the large grains are, from the standpoint of crystals in metals, more nearly normal than any others. They possess all the normal characteristics of well-formed crystals, just as crystals in properly concentrated salt solutions develop in easily recognized forms. Crystallization produced in metals in ordinary practice is more "abnormal" in that the grains are usually formed from what might be compared with supersaturated or undercooled solutions of salts.

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[2] *Trans.* (1916) **56**, 571.

DISCUSSION

F. G. SMITH.—Probably someone will ask whether I discovered why the bottoms of the large shells broke out. I did not, as a result of this investigation.

An experiment was made along the lines indicated in this paper, to determine whether abnormal grains greatly affected the physical properties of brass. Two ordinary test bars were annealed for ½ hr. at 750° C. and physical properties determined on one. The other was covered with indentations made with a peen hammer and then reannealed for 5 hr. at 750° C. It was found in the tensile test to be made up of large grains ¼ to ½ in. in diameter. The physical properties, however, differed from those of the first bar only as much as might be expected after a 5 hr. anneal under normal conditions. It appears then that the large grains produced in this manner do not ruin the physical qualities of the brass.

Electric-resistance Furnace of Large Capacity for Zinc Ores

BY CHARLES H. FULTON,* CLEVELAND, OHIO

(Chicago Meeting, September, 1919)

Description of Furnace and Process

Experimental work on the process was begun on a laboratory scale at Cleveland, Ohio, in 1914, and transferred to East St. Louis, Ill. in 1916, where a commercial sized furnace was in technical operation until January, 1918. The essential steps of the process are as follows:

Oxidized zinc ore or roasted zinc concentrate is mixed with crushed coke and coal-tar pitch and formed into briquets 9.25 in. (23.5 cm.) in diameter and 21 in. (53 cm.) long in a manner similar to that used in the manufacture of graphite or carbon electrodes, except that much less care and time are required. The composition varies with the nature of the ore; in one case, the composition was 100 parts ore, 70 parts coke, and 18 to 20 parts pitch. These briquets maintain their form and volume during and after the distillation of the zinc. This object is gained by using coke as the matrix and coal-tar pitch as the binder; this pitch becomes coke on heating and unites the ore particle and the original coke particle into a continuous mass. The briquet is an electrical conductor but only to such a degree that it can be used as a resistor.

The size of the ore, as in the present practice of zinc metallurgy, ranges from fine material, such as flotation concentrate, to coarse table and fine jig concentrate. The process is not restricted to any particular kind of ore, but is applicable to pure high-grade ores, ores high in iron, and complex zinc-lead ores, since the residue from the distillation is held immovably in place within the briquet. In the case of complex zinc-lead ores, the distillation is conducted with a carefully regulated temperature so that a high percentage of lead is retained in the distilled briquet, which may then be smelted for its lead content. In present zinc smelting practice, the reduction fuel is from 40 to 50 per cent. of the weight of the ore. In the briquet, it is from 60 to 85 per cent. of the ore; but unless the ore is exceptionally high in residue, the distilled briquet may be used over again as coke, or as a high ash coke for fuel purposes in power production.

Baked briquets are hard and tough and may be handled roughly

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without danger of breakage. In regular commercial work, they may be manufactured by means of extrusion or other suitable presses, after the manner in which electrodes are made, and the process be carried out continuously from the mixing to the finished briquet. The briquets weighed about 90 lb. (40 kg.) and contained approximately 50 lb. of ore, which

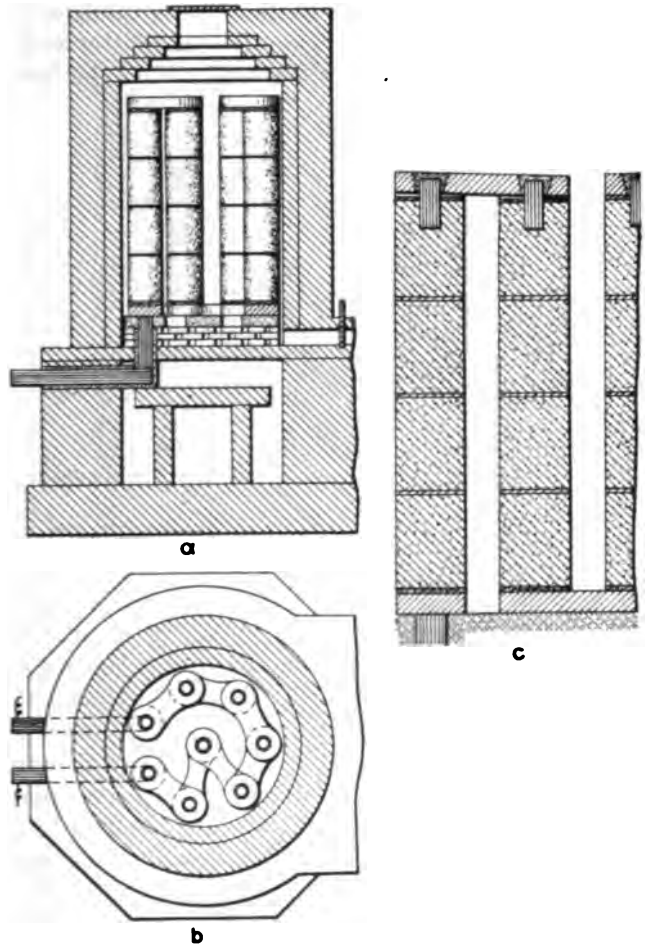


FIG. 1.—*a*, *b*, RETORT, ELECTRIC ZINC FURNACE; *c*, METHOD OF SETTING UP BRIQUETS.

is about the amount in a retort charge in present zinc-smelting practice. It is proposed to make briquets 12 in. (30.5 cm.) in diameter and 72 in. (183 cm.) long, which will weigh about 600 lb. (272 kg.). On distillation, the briquets lose from 30 to 50 per cent. of their weight, but maintain their form and volume. The zinc may be completely distilled from the briquet, traces only remaining, no matter what type of ore is used. The

completeness of distillation is due to the intimate mixture of ore and reducing agent maintained throughout the operation.

The second step of the process consists in making the briquet a part of an electric circuit and heating the same by an electric current to such a degree that the zinc is distilled. During this operation, the briquet is covered by a movable retort and the zinc vapor and carbon monoxide are conducted to a condenser in which the zinc is condensed. During the distillation, the briquet acts as a continuous resistor and maintains itself unaltered between the terminal electrodes. As the furnace is not

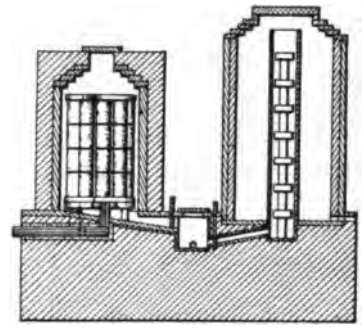


FIG. 2.—ELECTRIC RESISTANCE FURNACE AND CONDENSER.

limited to the interposition of one briquet between the terminal electrodes a large number may be interposed, thus giving a large unit furnace. While direct current may be used, alternating current is preferable on account of the ease of voltage control by means of transformers. The furnace at East St. Louis held a charge of 36 briquets, arranged in twelve columns of three each, set within a circle and operated on a three-phase circuit, four columns in each phase, connected in the customary Y connection. The amount of charge in this furnace varied between 3100 and 3200 lb. (1406 and 1451 kg.), the amount of ore being approximately 1700 lb. (771 kg.). The time of distillation was about 6 hr.; the total time, including the placing and discharging, was 8 hr., or three charges worked off in 24 hr. The capacity of the furnace was 5100 lb. (2268 kg.) of zinc concentrate per 24 hr. A proposed larger furnace, taking nineteen briquets weighing 600 lb. (272 kg.) each will have a capacity of about 8.50 tons of zinc concentrate per retort per 24 hr. Figs. 1 to 3 illustrate the principle of the furnace.

EARLY EXPERIMENTAL WORK

Experimental work was begun at the Case School of Applied Science, in Cleveland, in May, 1914, for the production of a zinc-ore briquet from which the zinc could be practically completely distilled, and leave the

briquet of the same volume and shape as before distillation. The experiments were carried on with all sizes of briquets ranging from 1 in. (2.5 cm.) in diameter and 1 in. long up to 9 in. in diameter and 20 in. long, and with spherical briquets up to 8.5 in. in diameter. Satisfactory briquets were made from practically every type of zinc-bearing material.

The "indestructible briquet" was intended for an automatic externally fired furnace,[1] but in 1915 experiments were begun using the

FIG. 3.—SET UP BRIQUET CHARGE. COLUMN 9.25 IN. DIAM., 66 IN. HIGH, 12 COLUMNS. *A*, BOTTOM GRAPHITE CONNECTOR BLOCKS; *C*, SPECIAL FIRECLAY BASE; *D*, TOP GRAPHITE CONNECTOR BLOCKS; *E*, GRAPHITE DISKS.

briquet as the resistor. The first briquets were 1 in. (2.5 cm.) in diameter and 1 in. long, but later the briquets were 3 in. in diameter and 4 in. long; the furnace held from 48 to 56 arranged in eight columns 6 or 7 briquets high, set up very much in the manner shown in Fig. 3 and operated in one continuous circuit. At first, direct current was used but later, alternating current. The distillation, in almost every instance, could be carried to completion, even with the many electrical contacts in the furnace, demonstrating that the indestructible briquet made a

[1] D. B. Jones: U. S. Patent No. 1292330.

perfect resistor if properly made. On the basis of this work the East St. Louis plant was planned, not as a commercial plant, but as an experimental plant for the purpose of working out the technical details of a commercial size furnace.

The Briquet

The briquet must form an intimate mixture of the roasted ore, reducing agent, and binder. A particle of ore should be in contact with a particle of reducing agent and both should be surrounded with a film of binder to unite all the particles into a coherent mass. In known applications of briqueting to ores, the briquet is destroyed during the operation that extracts the metal. In this particular case, the briquet must preserve its form and be practically of the same volume after the extraction of the metal as it was before in order to maintain passage of the electrical current. If the briquet should collapse during the distillation process, the furnace would become inoperative. Another advantage of the indestructible nature of the briquet, in the case of such ores as lead-zinc, zinc-copper, or Franklinite, is that the residue is in the form best suited for further metallurgical treatment.

The briquets are made with an excess of the reducing agent, coke, so that after distillation there will remain sufficient matter to maintain the original volume of the briquet. In general this condition is obtained if the weight of the distilled briquet is not less than 40 to 50 per cent. of the original briquet.

Zinc ores and zinc-bearing materials differ widely in the nature and amount of mineral residue left after the distillation of the zinc, as shown in Table 1. The nature and amount of the residue left by the ore has great influence on the stability of the briquet during and after distillation.

Table 1.—*Amount of Mineral Residue in Zinc Ore*

Name of Ore	Per cent. of Residue, by Weight	Character of Residue
Mascot, Tennessee	12.5	Largely silica with a little iron oxide.
Wisconsin ore, No. 1	15.8	Largely iron oxide, some silica.
Wisconsin ore, No. 2	18.3	Same as above.
Missouri ore	20.9	Largely iron oxide, some silica.
Canyon City, concentrate	27.9	Mostly iron oxide and silica.
Willemite zinc ore, from Franklin Furnace, N. J.	36.7	Mostly silica.
Franklinite zinc ore, Franklin Furnace, N. J.	55.58	Chiefly iron and manganese oxide.
Zinc dust, zinc oxide	None	

Coke Contents of Briquet.—Enough coke must be added to the ore to furnish the necessary carbon for the reduction of all the reducible oxides in the ore, plus such an amount that the weight of the briquet, after distillation, will be not less than 40 to 50 per cent. of the original briquet. Ores that leave a small amount of residue require more coke than ores that leave much residue. As the briquet must at all times be an electric conductor, there must always be present sufficient carbon in the coke, by which the current is chiefly carried.

The nature of the residue also is of great importance. If the residue is silicious in character, like that of the Willemite, which after distillation is in the form of comparatively sharp angular grains fused only on the edges, less coke is needed for a strong briquet than if the residue is of the nature left by Franklinite, which is in the form of round fused globules. The sharp angular grains are bound into a suitable network, with the coke grains, while the round fused globules must be held by the coke skeleton and in themselves give no strength to the structure they are part of. In the case of Franklinite, the residue consists largely of small globules of an iron manganese alloy, which aids in the conductivity of the mass; in the case of Willemite, the silicious residue is a non-conductor.

From the standpoint of non-conductivity, a lime residue is most objectionable as, under certain circumstances, this lime will form calcium carbide with the briquet giving rise to high resistance. An ore containing a high lime residue will make an excellent briquet that will act normally in the furnace until a certain temperature is reached, after which, due to the combination of lime and carbon, the resistance will increase and the briquet become locally overheated and break down. This difficulty can be overcome by an extra amount of coke. The proper amount of coke for different types of ores is, approximately, as follows:

	Per Cent. of Weight of Ore
Willemite[1]	30 to 40
Franklinite	70 to 80
Pure Mascot ore	70 to 75
Canyon City ore	60 to 70
Missouri silicate ore	85
Zinc dust	70

Pitch Content of Briquet.—The grains of ore and coke must be surrounded by a film of binder, which should have an appreciable thickness. As the binder must cover a certain amount of surface, the smaller the ore and coke particles the greater is the surface to be covered; therefore, the amount of binder varies directly with the fineness of the ore and coke.

[1] This proportion makes a strong briquet that will withstand distillation in an externally fired retort, but for electrical distillation the coke must be increased.

By experiment it was found that a satisfactory briquet can be made if the amount of binder is between 10 and 15 per cent. of the weight of the ore plus coke. More binder than this is detrimental, as the excess will be squeezed from the briquet during pressing; less, in most cases, will not give a satisfactory briquet. The percentages given apply to moderately fine ore, such as will pass through a 65-mesh screen, and to moderately fine coke, such as will pass through a 10-mesh screen. If the zinc-bearing material is excessively fine, as for instance zinc oxide or leaded zinc oxide, more binder must be used.

Size of Ore Particles.—Within certain limits, the size of the ore has relatively little influence on the final strength of the briquet; neither has it much influence on the rate of distillation of zinc from the briquet or the completeness with which the zinc is extracted. Ore that passes through a 10-mesh screen and 86 per cent. of which is coarser than a 35 screen, gives practically no different result from ore all of which passes through a 200-mesh screen. Usually the material furnished the zinc smelter is comparatively fine and sometimes very fine. Experiments with material coarser than 8-mesh have not been made. The ore or concentrate, usually, is made up of particles ranging from approximately $\frac{1}{10}$ in down to an extremely small size. This mixture is an advantage, although good briquets can be made from very fine ore. In the case of ores that give a fused residue in the form of little pellets or globules, as for instance, Franklinite, the coarser ore does not give as good results as the fine ore, as the first gives opportunity for these fused globules to segregate and coalesce within the briquet. Small globules are more permanently held in place by the coke skeleton. The size of ore particles has little influence on the ultimate stability of the briquets because the particle is practically destroyed during distillation, since it loses in the case of most zinc ores by far the greater part of its weight.

Size of Coke Particles.—The size of the coke particle has a very decided influence on the strength of the briquet. Very fine coke gives a much stronger briquet than moderately fine or comparatively coarse coke. For example, a cylindrical Franklinite briquet, 3 in. (7.6 cm.) in diameter, 4 in. (10 cm.) high, made with 100 parts ore, 70 parts coke, and 20 parts pitch, but in each case with different sizes of coke, had the following crushing strengths: 20-mesh, 15 lb. per sq. in. (1.05 kg. per sq. cm.); 48 mesh, 200 lb. per sq. in. (14.06 kg. per sq. cm.); 100-mesh, 610 lb. per sq in. (42.88 kg. per sq. cm.). When it is desired to obtain an especially strong briquet relatively fine coke should be used. However, as the coke increases in fineness and fine ore is used, the amount of binder will increase, which is undesirable from a commercial standpoint.

Character of Coke Used.—The coke used must be firm and hard, not soft and spongy. It should have a relatively low ash content, particularly if it is used with ore containing much residue. If it is to be used

with relatively pure ore, or with blue powder, the ash content may be high. Good, screened coke breeze, such as gashouse breeze or byproduct-oven breeze, is suitable if the ash content is not too high. Table 2 gives the screen size and ash content of crushed coke that has been successfully used in making briquets.

TABLE 2.—*Coke Data*

Screen Through	On Mesh	Percentage	Cumulative Percentage
	Connellsville		
..	10	0.13	0.13
10	20	13.28	13.41
20	40	33.88	47.29
40	60	14.50	61.79
60	80	11.19	72.98
80	100	5.60	78.58
100	120	4.05	82.63
120	150	2 50	85.13
150	200	2.27	87.40
200	...	12.60	100.00
Sulfur.....	...	0.35	
Ash.....	...	14.30	
	Coke Used at East St. Louis		
10	20	43.1	43.1
20	40	30.8	73.9
40	60	12.2	86.1
60	80	5.2	91.3
80	100	0.2	91.5
100	150	1.7	93.2
150	200	1.8	95.0
200	...	5.1	100.0
Ash.....	...	12.2	
	Gashouse-coke Breeze		
10	20	40.8	40.8
20	60	33.4	74.2
60	100	7.5	81.7
100	150	5.0	86.7
150	...	13.3	100.0
Ash.....	...	11.1	
	Byproduct-oven Breeze		
10	20	34.6	34.6
20	60	37.8	72.4
60	100	9.2	81.6
100	150	5.1	86.7
150	...	13.3	100.0
Ash.....	...	12.13	

Character of Pitch Used.—The character of the coal-tar pitch used is important. The chief points to be noted are the character of the coke left after the distillation of the volatile matter, the percentage of coke remaining after distillation, and the melting point of the pitch. In general, a high melting point pitch, 170° to 200° C., leaving a high percentage, 55 to 60, of good firm coke is best. Since the briquet is molded hot, and is taken from the mold while warm, it is weak, and the lower the melting point of the pitch the weaker is the briquet. A briquet made with a high melting point pitch is quite strong and stands handling when taken from the mold.

High melting point pitches obtained by mixing rather low melting point pitch with fine amorphous carbon will yield a high percentage of coke but they are weak and do not give good, permanent binding properties; neither have they good initial binding properties.

Table 3 gives data on the melting point and percentage of coke residue of a number of different kinds of pitch. The choice of the proper pitch is all important. High melting point pitch may be purchased in

TABLE 3.—*Types of Pitch*

Number	Type	Percentage of Coke	Character of Coke
1	Melting point, 82° C.	48.5	Good firm coke.
2	High melting point.	55.9	Very firm coke.
3	Melting point, 78° C.	50.2	Good firm coke.
4	Target pitch, high melting point.	59.7	Coke not firm.
5	Stiff flowing.	36.5	Good firm coke.
6	Melting point, 179° C.	53.0	Good firm coke.

a finely ground condition but frequently it does not possess the proper binding qualities and its use leads to failure in briqueting. It is desirable in all cases to test pitch experimentally before deciding upon its use.

Methods of Making Briquets.—A number of methods may be used for making briquets. The first method used in the experimental work was to thoroughly mix the coke, ore, and pitch (in powdered form) and heat this mixture, on a large hot plate, to between 175° and 200° C., or until yellow fumes appeared from the pitch, when it is granular and somewhat plastic, but not sticky. It was then molded in cylindrical steel molds, with a slight taper, the material being compressed by means of a steel plunger, the bottom of the mold being closed with a small disk to hold the material in place. The pressure varied between 500 and 1000 lb. per sq. in. (35 and 70 kg. per sq. cm.). For the best results the mold should have a temperature between 75° and 90° C. when a high melting point pitch is used. Under these conditions the briquet will come from the mold with a smooth exterior and sharp edges. The briquet, immediately

after expulsion from the mold, is somewhat weak but becomes strong and firm on cooling.

The second method, used for making briquets 9.25 in. (23.5 cm.) in diameter by 22 in. (56 cm.) long, employed at the East St. Louis plant, is as follows: The ore and coke in proper proportions are thoroughly mixed, slightly damp, in a knife-blade mixer and then stored in bins and fed as needed to a Bartlett-Snow kiln dryer, provided with plows. Here

FIG. 4.—BRIQUET PRESS.

it was heated to about 250° C. and discharged into a hopper at the end of the dryer, from which it was drawn into a hopper car in lots of approximately 500 lb. (226 kg.). This hopper was picked up by the crane and discharged into the knife-blade mixer, where the proper amount of molten pitch was immediately added and the contents mixed for 3 to 5 min., after which the mixture was discharged into a small, flat, brick-lined car kept at a temperature of about 250° C. This car was transferred to the tamping machine, made of a 3.25-in. (8.25 cm.) Ingersoll rock drill.

The tamping tool was a three-arm steel casting provided with cylindrical steel teeth 3 in. (7.6 cm.) long, which were replaced when necessary. The arms of the tamping tool freely cleared the sides of the mold, which was

made of heavy cast steel, in three parts longitudinally, the parts being held together, during molding, by hinged bolts fitting into slots. A specially shaped heavy steel base plate under the tamping machine insured a constant and fixed position of the mold during tamping. The bottom of the mold was closed by a steel disk, 1.5 in. (3.8 cm.) thick, which was set in a circular depression 1 in. deep in the steel base plate, causing the disk to project about 1 in. below the bottom of the mold while the walls of the mold rest on the base plate. The mold was then tamped nearly full of the mixture, which at the molding place has a temperature of 160° to 175° C. The mixture was fed into the mold by a long narrow scoop shovel and tamped in, the tamping and feeding being simultaneous. As the mold filled, the tamping tool was raised by the feed device of the rock drill.

The mold and its contents were then transferred to the adjacent finishing press, which was made from a railroad jack and used in the inverted position, see Fig. 4. A special plate under the jack permitted the mold to be placed accurately in position. The remaining space in the mold was filled with the mixture, a top steel disk put into place, and the contents of the mold compressed until the pressure reached 1000 lb. per sq. in. (70 kg. per sq. cm.), the pressure being determined by the contraction of the springs of the press. The weight of the mold and its contents, as it was placed under the press, rested on the bottom disk, which projected about 1 in. below the bottom of the mold. By this means both top and bottom pressure were obtained, which is preferable to pressure being applied from the top only. After the pressing, the bolts holding the mold together were slid out of place and the parts of the mold removed from the briquet, which was then placed on a car, where it was allowed to cool and become firm.

Small briquets have also been made on a laboratory scale by the method of "cold mixing." The ore and coke are mixed with powdered pitch and then moistened with zinc-sulfate solution and pressed into briquets. A typical mix is represented by 100 parts ore, 70 parts coke, 20 parts powdered pitch, and 20 parts of 5-per cent. zinc-sulfate solution. These briquets are fairly strong as they come from the mold and on baking become very firm. It is questionable whether they are as good as the hot molded briquets and the method has not been tried on a large scale.

Substituting Coal for Coke.—The base of the briquets is coke, but briquets have been made by replacing coke with coking coal, the idea being that the coking coal will furnish the carbon necessary for reduction and the excess required, as well as the binding effect of the pitch. Such briquets, however, require some binder and, after baking, are shrunken and warped; for this reason they cannot successfully be used in the elec-

tric furnace. The replacement of pitch by coking coal, if it were possible, would materially cheapen the briqueting process.

Briquets have also been made with anthracite coal, which were excellent from the standpoint of strength and non-warping quality; these briquets, however, do not become conductors of the electric current until a high temperature is reached, about 1150° C. This requires too great a degree of preheating. Ordinary coke briquets are conductors at 500° C.

Replacing Pitch with Coal.—Pitch in the briquet may be partly replaced by coking coal with good results. For instance, a mix made of 100 parts ore, 50 parts of 10-mesh coke, 40 parts of 80-mesh Pocahontas coking coal, and 10 parts powdered pitch, and one made of 100 parts of ore, 25 parts of coke, 70 parts of Pocahontas coking coal, and 10 parts of powdered pitch made good briquets after baking and gave good results on distillation. These briquets are made on the theory of replacing part of the coke and part of the pitch by coking coal, the coal acting as a binder and furnishing a part of the carbon; by this means the quantity of pitch required is reduced one-half. The proportions of coke and coal are calculated so as to leave the proper amount of excess carbon, taking into consideration the volatile matter of the coal. However, one serious objection to the use of any appreciable amount of coking coal is the fact that the products of the distillation of the coal are objectionable during the distillation of the zinc, and the relatively small saving of cost gained by its employment may be more than counterbalanced by the increased difficulties of condensation.

Baking the Briquets.—The purpose of baking the briquets is to coke the pitch; the temperature required to do this varies somewhat with the time of baking. For a 9.25 by 22 in. (23.5 by 56 cm.) briquet, a baking period of 6 hr., and 500° C. for 2 hr. near the finish, is about equivalent to a baking period of 8 hr. with a temperature of 450° C. for the last few hours of the operation. The briquets must be kept from oxidizing during the baking; that is, they must be under neutral or reducing conditions. Baked briquets have a density of 98 to 115 lb. per cu. ft. (1570 to 1842 kg. per. cu. m.) dependent on the ore, and on the proportions of the mixture.

At the East St. Louis plant, the briquets to be baked were stood on end on platform cars holding twenty briquets. Each briquet was set within a light sheet-iron cylinder 12 in. (30.5 cm.) in diameter and 26 in. (66 cm.) high, and the space between the briquets and the cylinders was filled with crushed coke. The car was then placed in one of the ovens, which formed part of the dryer. The two ovens were near the head of the dryer, which was the firing end. The products of combustion passed both over and below the baking oven by specially constructed flues. When a load of briquets had been baked, the car was withdrawn and replaced by

another. The period of baking was about 7 hr. and the maximum temperature, reached at the end, approximately 500° C. A briquet was baked for the proper length of time at from 450° to 500° C. is very hard and firm and may be thrown violently from the car to the floor while hot without injury. This was the practical test applied to one briquet from each car load.

The briquet during the baking passes through a weak stage, which is due to the condition of the pitch and continues during the baking until a temperature of about 300° is reached. From this temperature up to

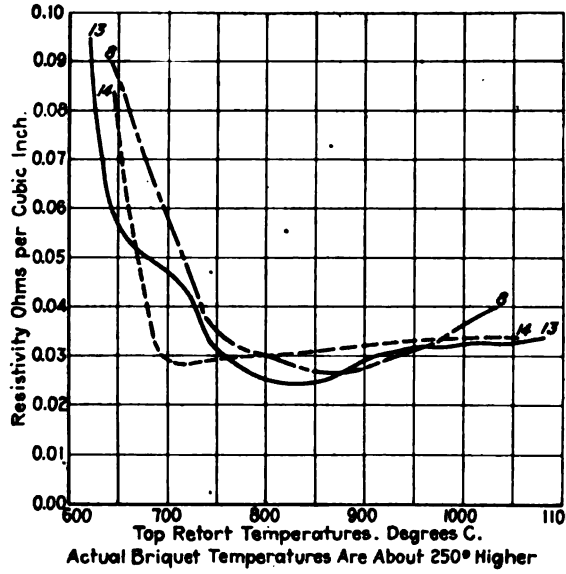


FIG. 5.—RESISTIVITY CURVE OF DISTILLING BRIQUETS.

500°, there is a constant increase in strength as the pitch becomes coked. It would be desirable to eliminate the baking of the briquets as a separate operation and conduct the process by placing the raw briquets on the furnace base and do the baking as part of the furnace operation. In the operation of the furnace, the highly heated retort from a finished charge is transferred by the crane to the new charge on the second base. The heat stored in the retort is sufficient to bake a charge of raw briquets but the weight of a column of briquets is such that the bottom briquet of the column would collapse in the weak stage. When the rate of heating is very rapid, a hard shell is formed on the briquets in the exterior columns of the furnace charge, immediately adjacent to the hot retort walls, before the interior becomes sufficiently heated to be weak; this shell will sustain the briquet during the critical stage. The interior columns of the charge, however, are heated more gradually from the retort walls and

do not form the hard shell, therefore they will collapse at the critical stage. It may be possible, under certain circumstances, to make a briquet that will not have to be baked in a separate operation.

Resistivity of Briquets.—The resistivity of hot briquets (900 to 1100° C.) depends on the amount of coke used and the nature of the residue of the ore; it will range from 0.015 to 0.04 ohms per cu. in. The resistivity of the raw briquet is very high (26 to 30 ohms per cu. in.). This resistivity drops slowly until the pitch is coked at about 450° to 500° C., when there is a sudden sharp drop to 0.6 to 0.7 ohms per cu. in. Fig. 5 shows a typical resistivity curve of distilling briquets.

Briquets made from ore, coke, and pitch become a practical conductor at between 450° and 500° C. Briquets in which part of the coke is replaced by bituminous coal do not become a conductor until a temperature of 620° C. to 750° C. is reached, depending on the proportion of coal used. Briquets where the coke is replaced by anthracite, do not become a conductor until about 1150° C. is reached. This is too high for the proper working of the process, for the briquet would have to be preheated, even after baking, to this temperature by means of the retort before the electric current would pass, and 1150° C. is the temperature at which distillation is very active.

The East St. Louis Plant

The large-scale experimental work was carried out in specially erected buildings in East St. Louis, Ill. The main building and annex thereto were constructed of steel and tile, the main building being of sufficient height to permit the operation of a 12-ton electric crane for the lifting of retorts and the handling of materials. The annex contained a small, complete machine shop, and part of the electric equipment. A separate small wooden building was provided for an experimental laboratory, and contained the small testing furnaces and the chemical laboratory. There were also bins and storage sheds for ores, coke, pitch and general supplies.

In one end of the main building was placed the coke crushing plant, consisting of a 7 by 10 in. (17.8 by 25 cm.) Blake crusher, a 20 by 12 in. (50.8 by 30.5 cm.) set of rolls, an inclined screen, and a return bucket elevator. Adjoining the crushing plant was a Bartlett & Snow kiln dryer, which dryed ore and coke, heated the ore-coke mixture, and contained two ovens for baking briquets. This dryer was fired at one end by an oil burner. The dryer was especially designed as regards the setting and served the various purposes indicated. In a commercially operated plant the drying, heating, and baking would be done in separate apparatus. Adjoining the dryer was the knife-blade mixer and the pitch melting kettle. Adjoining these was the tamping machine, briquet press, and tracks for the various transfer and platform cars for baking

couples) one at the top, and one at the bottom of the central chamber p and one at the bottom of the outer annular chamber. The retort was provided with two pyrometers, embedded within the refractory lining

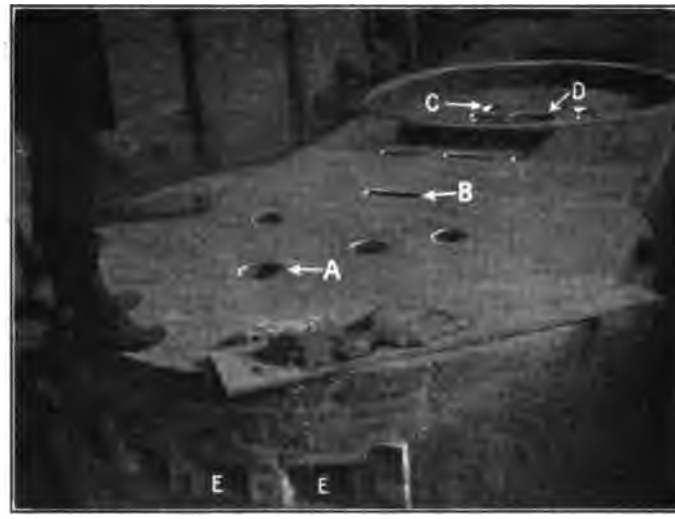


FIG. 8.—BASE OF FURNACE C.

FIG. 9.—ELECTRODE CONSTRUCTION, FURNACE C.

within ½ in. (12.7 mm.) of the interior surface, one at the top and one at the bottom. The readings of the retort pyrometers were about 250° to 300° C. below the actual briquet temperature but, with this correction known, served as a perfect guide in the operation of the furnace.

Details of Construction.—The retort consisted of a 0.25-in. (6.35 mm.) steel shell stiffened at the top by a 12-in. (30.5-cm.) channel, to which were bolted heavy cast-steel hooks, which engaged the chains of the bail by means of which the retort was lifted by the crane. The bottom of the shell was drawn in 1 in. and then flanged outward for stiffening; the contraction was for the purpose of holding the refractory lining firmly in place. The bottom of the lining was a circle of firebrick blocks 9 in. (23 cm.) high and 13.5 in. (34 cm.) wide, the full thickness of the lining. On these was built the interior lining of high-grade firebrick, 4.5 in. (11.4 cm.) thick, the space between these and the steel shell being filled with 9-in. sil-o-cel brick and loose sil-o-cel. The roof was a firebrick dome, covered with loose sil-o-cel. The interior diameter was 48 in., and the interior height from the base to the lowest point of the dome was 72 in. The clearance between the briquet columns and the lining of the retort was 2.5 in. The clearance between the columns was about 2 in.

The electrode construction is shown in Figs. 8 and 9. Four graphite electrodes *F*, Fig. 9, 6 in. square and finished to cylindrical ends for the attachment of the electrode holders *G* passed into the furnace base through the opening *E*. On these electrodes were set 6-in. graphite risers, which reach the level of the furnace base through the openings *A*, Fig. 8. These plugs were later replaced with 9-in. plugs. A seal was made by filling in the space between the plugs and the walls of the openings with finely crushed carbon. In the first operation of the furnace, a special firebrick block was set on the base of the furnace, as shown at *C*, Fig. 3, through which the vertical plugs passed to make contact with the graphite blocks *A*, on which the columns of briquets were set. The purpose of this firebrick was to prevent a short circuit in the case of a condensation of zinc on a cool base. It was found unnecessary so the graphite blocks *A* were set directly on the base in contact with the vertical riser plugs. A charge as set up is shown in Fig. 3.

The top connections are made by 5-in. graphite blocks *D*, as shown in Fig. 3. Fig. 7 shows the arrangement of the bottom blocks and of the top blocks on the "Y" connection. As shown in Figs. 8 and 9, the furnace has four electrodes. One of these is the neutral, which is brought to the exterior of the furnace to provide for an extra connection in case of a breakdown.

In order to insure perfect contact between briquets, a paste consisting of 50 parts tar oil and 35 parts of finely ground graphite was rapidly applied, hot, to the ends of the briquets by a stiff broad brush or a trowel. It had excellent adhesive properties and when baked was as good a conductor as the briquet. A number of charges built up of whole briquets and briquets broken into a number of pieces, making numerous contacts with the use of this contact material, passed through the distillation

perfectly. This is a very severe test of the process from an electrical standpoint.

In setting up a charge, a 0.75-in. (19 mm.) graphite disk, the diameter of the briquet, was placed on the graphite block *A*, Fig. 3, and thinly coated with contact material, then the first briquet placed in position, its top coated with contact material, then the next briquet was placed in position and its top coated, then the third. This last briquet had a 2-in. (5 cm.) hole at the center, 2.5 in. deep, which was formed at the time of pressing the briquet by the top pressure plate, which was fitted with a slightly tapered pin. After the twelve briquet columns were placed in position, 1.75-in. (4.4. cm.) graphite pins were dropped in place in the top briquet, contact material applied, and 1 in. graphite disks, with a 2-in. hole at the centers slipped into place, and the top connectors placed into position. The top connectors, 5 in. thick, were provided with tapered holes somewhat larger than the pins, into which the projecting pins fitted. The space between the pins and the walls of the holes in the connectors was filled with finely crushed coke. By this system the briquet columns were held firmly in position and the slight shrinkage and motion in the charge provided for.

The method is shown in detail at *c*, Fig. 1. A charge was set up in from 2 to 3 hr. by two men. In the making of the briquets care was taken to have their ends parallel and perpendicular to the axis, and all approximately of the same length. The length sometimes varied slightly, in which case and when briquets broken in the handling were used, deficient height of column was made up by the use of extra graphite disks.

After the charge was set up, a fireclay luting was spread, ring form, on the base and the retort was lowered into position by the crane. The luting made a tight joint. The exit hole at the top of the retort, was left open for a short time after power was applied at the electrodes, to permit the escape of pitch fumes and the first gases, after which it was closed and the valve *x* (Fig. 6), leading to the vapor box and condenser opened. In Fig. 8, the passage from the base to the upper chamber of the vapor box *o*, Fig. 6, is shown at *B*. From the vapor box, the gases passed to the central condensing chamber *p* of the condenser, thence by the cross passage *k* to the outer annular condensing chamber, which was divided, by vertical walls, into four compartments in series, the carbon monoxide finally burning at an exit at the top of the last one. The central condensing chamber drained into the vapor box, and spelter in furnace C was tapped from the vapor boxes. In the operation of this furnace, practically nothing was found in the annular condensing chamber except a very small quantity of blue powder. This chamber was provided with tap holes at the bottom. The retort ends of this furnace were satisfactory, but the condenser was too complicated. The condensation was excellent as regards the non-formation of blue powder. After six charges,

the condenser was found to be practically free from blue powder and dross. At no time did the gas flame show more than the permissible amount of zinc. Some zinc was lost by leakage at the cross passage from the central to the annular chamber, which could not be kept tight. The bottom of the vapor boxes also could not be kept tight, and spelter escaped in considerable quantity into the base and ground beneath the base. It was decided that the condenser would have to be a simpler structure and that the passage from the retort to the condenser must be simple, short, and easy of access for the purposes of cleaning. The new design gave rise to furnace D.

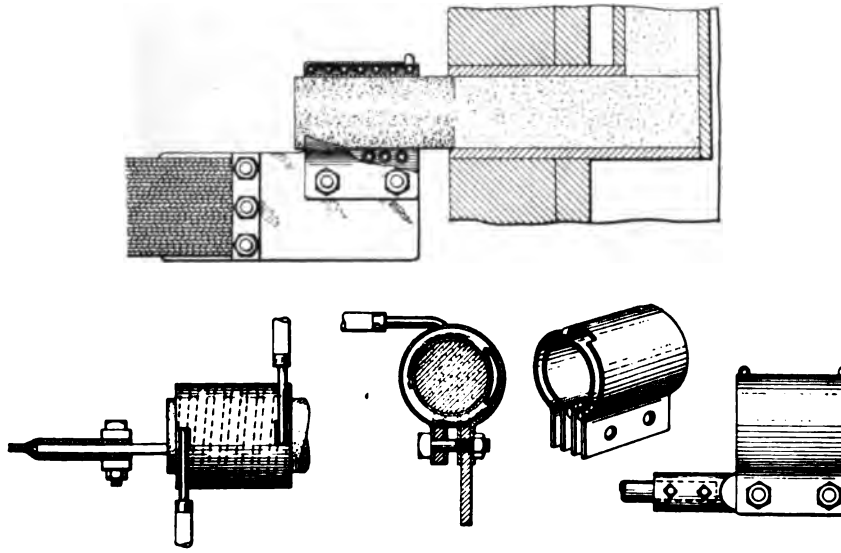


FIG. 10.—JACKSON ELECTRODE COOLER.

The electrical equipment for furnaces C, D, and E was the same and consisted of a General Electric 150-kw., three-phase transformer and a polyphase induction regulator. Sixty-cycle current at 1300 volts was stepped down to 220 volts by transformers outside of the building and passed to the regulator placed in one corner of the main structure. From this, cables in underground conduits led to the transformer pits located at the end of each retort base. The transformer was placed in this pit and connected to the primary cables from the regulator and the secondary leads of the transformer to the furnace electrodes. When a charge was distilled, the connections were broken and the transformer lifted by the crane and transferred to the pit at the other retort base. The secondary terminals of the transformer were brought out to a terminal board attached to the transformer and were so arranged by means of heavy copper links, which could be rapidly changed in position, that the

three main secondary taps leading to the electrodes of the furnace by heavy flexible cables, could be at voltages of 27.5, 55, 110, and 220. By means of the regulator, the voltage adjustment between these ranges was practically continuous and a maximum voltage of 262 and a minimum of 22.5 could be obtained with a primary line voltage of 220. The power company employed boosters on its line so that a line voltage of 300 volts was sometimes available. The voltage at the electrodes with the Y set up was, when beginning operations with a cold charge, sometimes as high as 300. With hot retorts, however, the voltage would be about 150 at the start, with an energy input of 120 to 150 kw., lowered to from 75

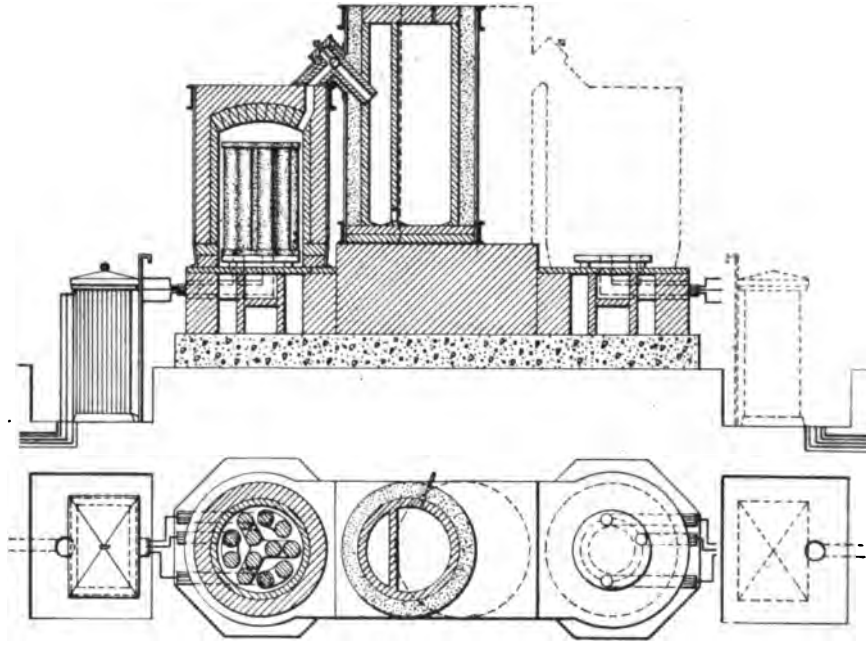


FIG. 11.—FURNACE D.

to 90 during distillation. The energy input used was from 122 to 184, the latter for only short periods of time as this intensity overloaded the transformer. The electrical equipment was somewhat under capacity and the furnaces could easily take 200 to 250 kw., as was demonstrated later with new equipment on furnace F. The low kilowatt input for furnaces C, D, and E accounts for the somewhat higher distillation periods (more than 8 hr.) and also the larger power consumption, due to increased radiation losses on account of the unnecessarily long time. All electrical instruments and switches were located in the shop annex, and the furnace was electrically operated from this place. The electrode holders and coolers were specially designed[3] for the purpose and are shown in Fig. 10.

[3] R. O. Jackson: Patent No. 1242554.

Furnace D.—This furnace differs from furnace C in the design of the condenser. The same principle was used, but there was no heating of the retort base or the condenser. Fig. 11 illustrates the arrangement. Instead of a bottom connection from the retort base to the condenser, a top connection, shown in Fig. 12, was permanently attached to the condenser.

After the retort was placed in position, the condenser was lifted by the crane and swung into position so that the opening of the connection registered with the opening in the top of the retort. Luting was then placed

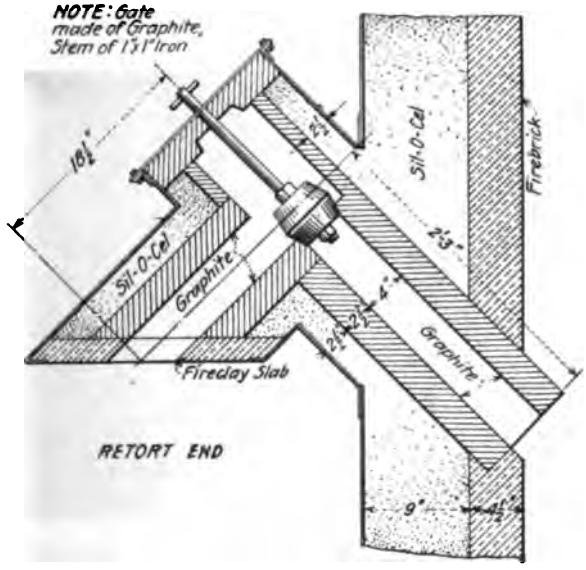


FIG. 12.—TOP CONNECTION FOR ELECTRIC FURNACE.

around the retort opening and the condenser gently lowered to its base; this made a tight joint between the condenser and retort. When the charge was distilled, the transformer was transferred by a crane to the second retort base, the valve of the condenser connection closed, and the condenser lifted by the crane, swung around 180°, and set on the center of its base. The retort was then lifted about 3 in. (7.6 cm.) and pulled toward the center of the building; this swept the distilled briquets to the floor over an apron plate, as shown in Fig. 13. The retort was then transferred to the other charge, the condenser set by the crane, and distillation begun on the second charge. A new charge was set up on the first base, the men being protected from the hot base by asbestos mats and shoes.

The connection was designed so that it could be readily cleaned out by the removal of the cover-plate over the graphite plug valve. The connector is by no means a perfect device and had to be cleaned every

second charge, especially if the valve was not carefully closed at the end of the run. The passages also are somewhat small.

The condenser was made of the same shell as furnace C, except that a steel bottom was riveted in place. It was lined first with 9-in. (23 cm.) sil-o-cel brick followed by 4.5-in. of high-grade firebrick. Its interior diameter was 42 in. and its interior height 9 ft. It had a longitudinal partition of firebrick wall, as shown in Fig. 11, and was known as a two-pass condenser. For the initial charge, the condenser was heated by an oil burner placed into an opening at the top, the products of combustion traveling down the large pass, up the small pass, and out of the connection as a flue. Preliminary tests showed that if the condenser

FIG. 13.—APRON PLATE AND DISCHARGED BRIQUETS.

was heated to 940° C. and then closed and allowed to stand the temperature dropped from 940° to 630° C. in 16 hr. It was later found that this radiation about balanced the heat input, due to the condensation of zinc vapor, and the condenser maintained itself at a temperature of about 700° C. at the inlet and 500° C. at the exit. With more rapid working, it would probably have been necessary to spray the exterior with water. With less rapid working the condenser would undercool, as was the case when less than two charges were distilled in 24 hr.

Charges 7, 8, 9, 10, and 11 were distilled with this condenser, when the bridge wall collapsed at the top, at which point the temperature was about 500° C. This collapse was due to carbon deposition within the firebrick localized at the iron-oxide spots of the brick. The action is due to the decomposition of carbon monoxide at the temperature existing and is elsewhere described.[4] The condenser was then repaired, the bridge

[4] C. H. Fulton: Condensation of Zinc from its Vapor. *Trans.* (1919) **60**, 280.

wall being replaced by a 30-in. (76-cm.) cylindrical flue tile, for a second pass. The condenser was again brought to the desired temperature by the oil burner and charges 12, 13, and 14 run, when part of the condenser brickwork, including the top tile, collapsed for the same reason as before.

The condenser, when opened after each run, showed no blue powder, the walls were covered with spelter in the form of droplets, and this in places was coated with a thin layer of dense rock oxide. There was some zinc dross in the bottom. The complete metal balance of these two runs is given in Tables 4 and 5. In the first run 42.7 per cent. of the zinc content of the charges was recovered as cast spelter bars; and in the second run 52.6 per cent. This recovery was from a practically new furnace in each instance.

TABLE 4.—*Metal Balance*

RUNS NOS. 7, 8, 9, 10, AND 11, MAY, 1917

ZINC IN BAKED BRIQUETS	POUNDS
Each charge	573.0
Zinc in five charges, total charged	2855.0
ZINC REMAINING IN DISTILLED BRIQUETS	
Run No. 1, 2.36 per cent	52.4
Run No. 2, 0.67 per cent	14.0
Run No. 3, 1.80 per cent	39.0
Run No. 4, 0.93 per cent	19.4
Run No. 5, 5.97 per cent	151.0
Total zinc in distilled briquets	275.8
Zinc cast as spelter	1242.5
Zinc in scrapings from bridge wall, rechargeable @ 41.75 per cent. zinc	899.0
Zinc in brick from condenser, @ 1.74 per cent. zinc	115.3
Zinc unaccounted for	322.4

SUMMARY

	PER CENT.	POUNDS
Spelter tapped	42.7	1242.5
Scrapings, rechargeable	30.8	899.0
Zinc in brick from condenser	3.9	115.3
Zinc in distilled briquets	9.1[a]	275.8
Unaccounted for	13.5[b]	322.4
	100.0	2855.0

[a] The amount of zinc left in briquets is entirely at the will of the operator; this is shown on the individual runs. The runs in this series were, in part, undertaken to obtain figures on power consumption, and certain runs were discontinued at given power inputs to determine proper point of stopping.

[b] This covers zinc absorption in retort hood, base, and passageways and includes zinc escaping uncondensed.

TABLE 5.—*Metal Balance*

RUNS NOS. 12, 13, AND 14. MAY 9–11, 1917

ZINC IN BAKED BRIQUETS	POUNDS
Each charge	573.0
Total zinc in three charges	1719.0
ZINC REMAINING IN DISTILLED BRIQUETS	
Run No. 12, 6.57 per cent	169.0
Run No. 13	Nil
Run No. 14, 0.131 per cent	2.6
Total zinc in distilled briquets	171.6
Zinc in scrapings from condenser, rechargeable @ 60.85 per cent. zinc	496.0
Zinc cast as spelter	903.5
Zinc unaccounted for	147.9

SUMMARY

	PER CENT.	POUNDS
Spelter tapped	52.60	903.5
Scrapings, rechargeable	28.80	496.0
Zinc left in distilled briquets	9.83[a]	171.6
Unaccounted for	8.77[b]	147.6
	100.00	1719.0

[a] The amount of zinc left in briquets is entirely at the will of the operator; this is shown in the individual runs. The runs in this series were in part undertaken to obtain figures on power consumption, and certain runs were discontinued at given power inputs to determine proper point of stopping.

[b] This covers zinc absorption in retort hood base and passageway, and condenser brickwork, and includes zinc escaping uncondensed.

The destruction of the condenser lining also took place with furnace E. It became evident, therefore, that the condenser lining would have to be made of refractory material free from iron. The only real difficulty in the condensation was the destruction of this lining at a temperature of about 500° C. At higher temperatures the destruction is not noticeable, as the condenser failed only in the parts where this temperature existed. In the retort, lined with the same firebrick, no destructive action was noted; in fact the retort lining was not repaired at any time that the plant was in operation. It is probably not possible to operate any large zinc condenser for a long period, even though every precaution is taken in construction and operation to keep it tight against air. One of the underlying ideas in a condenser of this movable type is to operate it as long as it is in good condition, then replace it with another one at the proper temperature and clean and reheat the first one.

TABLE 6.—*Electrical Records of Run 14*

Time	Electrode			Primary			Primary			Indicating Wattmeter		R.W.H.M.*	Pyrometer Reading, Degrees C.				
	Volts Per Phase			Volts Per Phase			Amperes Per Phase						Retort		Condenser		
	1–2	2–3	3–1	1–2	2–3	3–1	1	2	3				Bottom 1	Top 2	Top 4	Bottom 5	
6:15	290	290	290	290	290	290	150	150	100	...	...	1508.0	...	...	...	...	In at 5:50 A. M., 220 volt. connection
7:00	121	118	132	126	126	130	480	425	260	...	...	1510.5	...	...	...	...	
7:30	117	112	120	120	122	122	590	540	460	...	...	1512.0	...	..	...	...	
8:30	134	131	132	271	256	266	445	430	375	255	225	1513.0	480	640	650	520	
9:00	67	64	65	138	124	128	280	310	300	80	90	1515.0	460	650	630	520	
9:30	96	86	93	196	181	192	615	615	615	255	255	1517.0	500	670	610	560	Flame lit at condenser.
10:00	79	72	75	162	150	158	650	650	660	215	230	1520.0	520	680	610	585	
10:30	68	65	65	142	134	134	650	595	660	175	200	1522.0	530	690	660	610	
11:00	62	59	60	130	124	124	650	600	650	165	185	1525.0	540	690	670	600	
11:30	63	60	59	130	124	122	645	550	650	150	180	1527.0	550	710	670	590	
12:00	63	58	61	132	128	126	650	600	655	165	190	1529.0	570	730	670	590	
12:30	65	61	62	136	128	128	680	620	680	175	195	1531.0	570	730	...	...	
1:00	65	61	61	134	128	126	655	595	665	165	180	1534.0	550	720	...	...	
1:30	67	62	63	139	130	128	680	620	650	170	180	1536.0	520	680	...	...	
2:00	64	61	62	134	128	128	635	580	640	165	185	1538.0	490	670	...	...	
2:30	65	61	62	126	128	128	620	565	620	165	180	1541.0	490	660	...	...	
3:00	65	60	62	134	128	128	620	600	620	165	175	1543.0	775	920	...	470	
3:30	66	61	63	140	130	130	590	600	610	160	180	1545.0	780	930	...	470	
4:00	66	62	65	140	130	130	570	600	620	160	180	1547.0	780	940	...	480	
4:30	65	62	63	140	130	130	610	570	610	170	160	1549.0	790	960	...	480	
5:00	69	67	65	142	138	136	590	490	610	150	180	1552.0	800	970	...	480	
5:30	67	65	65	140	136	170	600	520	600	155	180	1554.0	800	990	...	480	
6:00	68	65	65	140	138	138	600	520	600	160	175	1556.0	820	1010	...	490	
6:30	69	67	65	140	138	136	590	550	590	155	175	1558.0	840	1030	...	490	
7:00	70	67	67	144	140	138	600	520	600	165	188	1560.0	850	1045	...	488	
7:30	73	70	71	154	146	144	620	550	620	180	200	1562.0	860	1060	...	490	
8:00	74	71	71	152	143	146	620	520	600	175	190	1565.0	875	1085	...	480	
8:30	74	70	70	152	144	144	600	560	590	165	185	1567.0	900	1110	...	470	
9:00	74	69	71	150	142	144	600	560	580	180	185	1570.0	920	1130	...	470	Power off at 9:10.
9:45	75	70	72	152	144	144	560	530	560	175	180	1571.0	935	1110	...	470	Power on at 9:45. Power off at 9:50.

* Recording watt-hour-meter. For kw.-hr. multiply by 33⅓.

In Table 6 is given the electrical record of run 14, which is typical. It will be noted that the balance of the phases is good; in many runs it was still more even. The power factor ranges between 88 and 91. The total time was 15.5 hr. The average input was 143 kw., which is too low, but all that was available. The power consumption was 2109 kw.-hr. for the charge, which is equal to 2576 kw.-hr. per ton of ore. This is higher than necessary as later work demonstrated.

As charge 14 was the last of a run, it was allowed to cool with the retort in place, and the briquets of every other column weighed, sampled and analyzed. The record is as follows:

Twelve columns of briquets, three each. Total height of all columns, 763 in. (1928 cm.). Weight of undistilled charge 3161 lb. (1433 kg.). Density of baked briquets, 4.15 lb. per lin. in. Density of distilled briquets, 2.82 lb. per in. Baked briquets contained, 18.2 per cent. zinc. Total zinc in charge, 573 lb. Total zinc in distilled charge, 0.131 per cent., or 2.6 lb. Weight of ore in charge, 1630 lb.

Sample	Weight Distilled Briquet, Pounds	Length, Inches	Per Cent. Zinc
Column 1, top	59.0	21.00	Nil.
Column 1, bottom	62.0	21.60	0.05
Column 3, top	61.0	22.00	0.08
Column 3, middle	60.0	21.50	....
Column 3, bottom	62.5	21.75	0.54
Column 5, top	60.5	21.50	Nil.
Column 5, middle	62.0	21.75	....
Column 5, bottom	59.5	21.25	0.43
Column 7, top	61.5	21.60	Nil.
Column 7, middle	60.0	21.60	....
Column 7, bottom	58.5	21.00	0.19
Column 9, top	60.0	21.50	Nil.
Column 9, bottom	58.5	20.75	Nil.
Column 11, top	....	.....	Nil.
Column 11, middle	58.5	20.75	Nil.
Column 11, bottom	57.0	20.75	0.28

The density of the briquet is a measure of the distillation. The above charge lost 32 per cent. of its weight; this is the proper loss for complete distillation with the briquets used, which were made of 100 parts Missouri silicate ore, 35.5 per cent. zinc, 85 parts coke, and 18.5 parts pitch. A loss of 34 to 40 per cent. may take place when the charge is overdistilled, in which cases only traces of zinc can be detected in the distilled briquets. In Fig. 5 are shown the resistivity curves of charges 8, 13, and 14; these are typical of briquets made of Missouri silicate ore. Toward the end of the operation the resistivity rises somewhat; and this rise indicated

at the instrument board as a drop in amperage with no voltage change, indicates the end of the distillation period.

The distilled charge was discharged from the retort base by slightly lifting the retort and then pulling it sidewise by means of the crane. The bottom graphite electrode blocks stay in place, but the top ones, are of course, swept off with the charge. They are at once drawn from the mass of briquets and covered with crushed coke. Graphite does not oxidize readily at a low red heat, and there was very little wear on the connector blocks during the operation of the plant. The bottom blocks on the base, immediately after the discharge of the briquets, were thinly covered with crushed coke, spread by a big shovel. After an hour the base cooled to or below a dull red, when it was cleaned off by a stiff broom and a new charge set up. The discharged briquets on the floor were quenched with water and then removed. With furnace F, the base was higher and the briquets were discharged directly into a steel car, quenched, and removed to the dump.

Connectors Made of Briquet Mixtures.—Experiments have been made with a small scale laboratory distilling furnace, with 1¾-in. diameter briquets, in which the graphite connectors were replaced by connectors molded from briquet mixture, modified by the addition of somewhat more pitch and the use of finer coke to give additional strength. These experiments were successful and it was the intention to make full size connectors of this type, when the work had to be discontinued. Both bottom and top connectors of this kind were to be employed, thus increasing the capacity of the retort, and doing away with the use of all graphite except the electrodes proper, which are not subject to wear. It will be noted that even with the use of graphite connector blocks, there is no regular or fixed electrode consumption in this furnace.

Use of Distilled Briquets.—The distilled briquets may be used again as coke. In the briquet charges distilled in furnace F, some of the briquets were made by replacing 50 per cent. of the coke by 70 per cent. of distilled briquet. These caused no difficulty in the distillation, although the distilled briquets are a most unfavorable material on account of the very high percentage of residue in the ore. The distilled briquet is practically a coke containing 34.5 per cent. ash, which high ash content would not be present with ordinary zinc ores in the briquet.

Heat Capacity of Retort.—The initial heating of the briquet charge on the retort base is done by the heat stored in the retort from the last charge. Fig. 14 gives the curves representing the heat capacity of the retort and the standard charge expressed both in calories and kilowatt hours, for different temperatures.

Furnace E.—Furnace E differs from furnace D in having a bottom connection between the retort base and the condenser, this connection being part of the condenser. In order to arrange for this construction, the

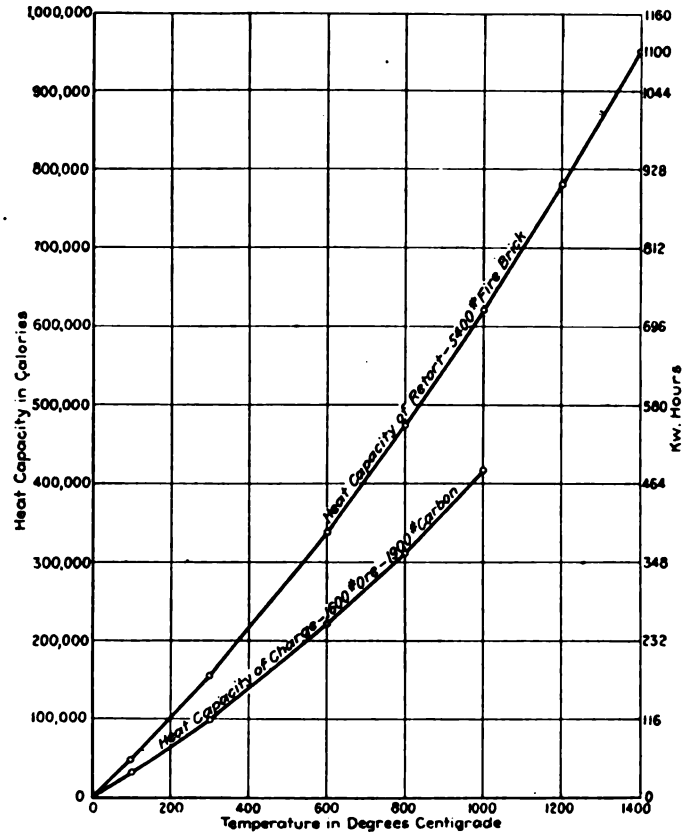


FIG. 14.

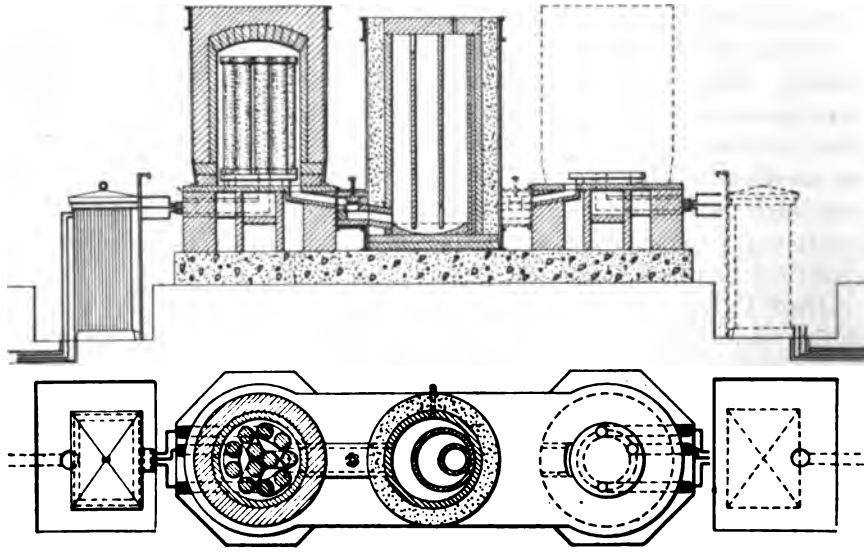


FIG. 15.—FURNACE E.

central part of the furnace base, which had served as a condenser support, was removed and the old passageway for zinc vapor in the retort base rebuilt. Grooves were also cut in the retort base immediately around the graphite base blocks, which drained into the vapor passage. It was thought, in the operation of furnace D, that in the earlier stages of the operation metal sometimes condensed on the walls of the retort and drained to the base, giving rise to redistillation, which prolonged the time and increased power consumption. The results obtained with furnace E do not prove this to be true. From the construction standpoint, however, there are certain advantages in a bottom connection.

In the operation of the process, the retort from a distilled charge is usually between 1100° and 1200° C. but sometimes cooler. The ideal condition for operation is one in which the retort wall temperature is always higher than the charge temperature, which can be obtained by working with good hot retorts and by rapid distillation.

Furnace E is shown in Fig. 15. It was operated in the same manner as furnace D and the results with it were about the same. The condenser was a three-pass one, the passes being made of flue tile, as shown. After nine charges, the condenser broke down in the same way as the furnace D. No metal balance was drawn up on this run. About 60 per cent. of the zinc in the charges was recovered as cast spelter, over 1100 lb. (498 kg.) being drawn from the condenser at one tap. When the condenser was opened, the walls were heavily coated with metal drops, dross, and dense rock oxide, and there was considerable dross in the bottom, but no blue powder. Once or twice during the campaign, the condenser valve was open during the change from base to base and air passed through the condenser, a highly undesirable condition.

Furnace F.—This was the furnace constructed for operation in connection with the new electrical equipment, consisting of three 870-k.v.a., single-phase transformers, switch connections and instrument equipment. The furnace consisted of three adjoining retort bases, two distilling retorts (identical with those used for the former furnaces), a movable combination condenser for spelter, blue powder, and oxide, and one of the old retort bases reconstructed to preheat retorts by means of oil burners. The electrical equipment was designed for extra capacity, so that it could be used in proposed subsequent work on larger units with 12-in. briquets. The foundation of the bases was built of concrete and contained a tunnel for the bus-bars from the transformers. The transformers were set as close as possible to one end of the furnace, in a shallow pit, which had waste connections to take care of the cooling water. The bases proper consisted of rectangular steel boxes filled with a firebrick arch, containing the opening for the electrodes and, on one side, a vapor passage leading to the condenser connection.

The idea was to have extra bases to form the top of the cars on which

the charge of raw briquets would be set up, with the connectors in place. The cars would then be passed into the ovens and, after baking, removed, and the base with its charge heated to a temperature of 500° to 600° C. picked up by crane and set on the furnace and at once distilled, thus conserving the heat energy in the hot baked charge. The movable base also served as a cover for a flue system under the base and surrounding the electrodes, which was heated by an oil burner located on the opposite side to the vapor passage. The exit flue from this system emerged from each base below the vapor passage and the products of combustion were passed to a heating chamber in the spelter condenser, to preheat this for the start of operations. This base-heating system was, in effect, the

FIG. 16.—BASES OF FURNACE F.

same as was used in furnace C. It was found to warp the bases and to be unnecessary, as in the case of furnace C, and was not used in subsequent operations. The electrodes were 12 in. (30.5 cm.) in diameter, supported on jacks in the tunnel underneath the bases, and passed through the openings in the base, the seal between the electrodes and the openings being made by crushed carbon. The jacks afforded a ready means for slightly raising or lowering the electrode to keep it level with the top of the base. Fig. 16 shows the construction of furnace F.

The condenser proved unsatisfactory and was to be replaced with the style used on furnaces D and E. Experiments in making zinc dust were successful, but the experiments in making oxide failed in the collecting device used. Before the style D and E spelter condenser could be again used the war conditions stopped experimental work.

The electrical system was such that the primary leads to the transformers could be connected either in delta or in Y, and the secondary leads could be brought out either in delta or in Y connection. By means

of switches on the primary side, a wide range of voltage by small steps could be obtained at the electrodes. The current used was 40-cycle 13,000 volts primary, from Keokuk dam on the Mississippi River. Fig. 17 shows the wiring diagram of the three single-phase 870-k.v.a. transformers, and Fig. 18 the various connections of switches, the k.v.a. capacity of the transformers obtainable with the different connections, and the corresponding voltage at the electrodes of the furnace. The power was applied at the electrodes by means of water-cooled electrode holders of the design already shown.

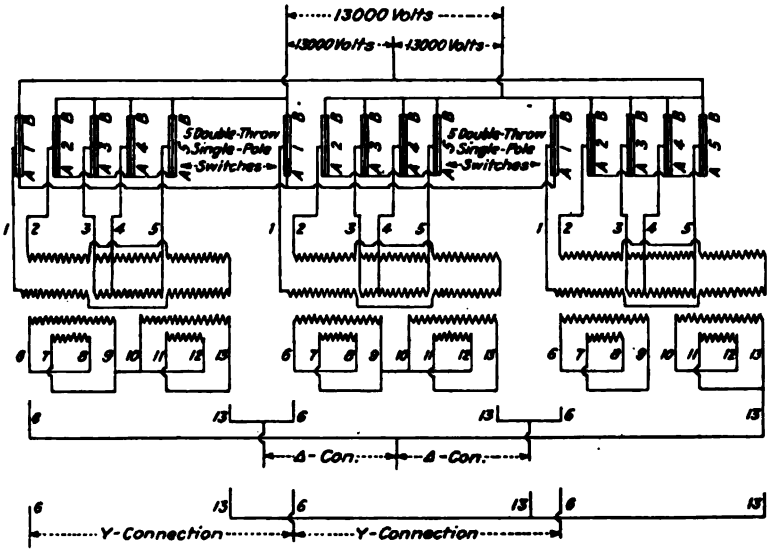


FIG. 17.—WIRING DIAGRAM 870 K.V.A. TRANSFORMERS.

Operating with Preheated Retorts.—In the furnace as at first operated, in the initial charge of any run, the retort was heated by radiation from the briquet charge, and when transferred after the distillation to the second charge was at a temperature of from 1000° to 1200° C. The initial charge therefore always showed the extra power consumption necessary to heat the retort to this temperature. The ideal condition is to have the heat radiated from the retort walls to the charge rather than from the charge to the retort, which means working with hot retorts. In the case of high cost of electrical energy, the process lends itself readily to a method of working in which the retort is preheated to a temperature of 1250° to 1350° C. by means of a regenerative system of preheating bases fired by gas. The use of the preheated retort reduces the time and power consumption. To the electrical power consumption in this case must, of course, be added the cost of preheating; but the electrical power consumption will be reduced by virtue of the shortened time, as this cuts down the radiation losses. In the operation

of furnace F, preheated retorts were used. One of the old furnace bases was arranged for this work, the retorts being preheated by oil. In Table 7 are given the results obtained.

HIGH-VOLTAGE COILS, DELTA CONNECTIONS

K.v.a.	Connections	Voltage of Secondary Coils, Delta Connection	Voltage of Series-multiple Coils, Y Connection
495	2 to A, 3 to A, 1 to B & 5 to B	99	171
530	2 to A, 4 to A, 1 to B & 5 to B	106	184
580	2 to A, 3 to A, 1 to B & 4 to B	116	200
640	2 to B, 3 to B & 1 to B	128	222
695	2 to A, 4 to A, 1 to B & 3 to B	139	240
770	2 to A, 5 to A, 1 to B & 4 to B	154	266
870	2 to A, 5 to A, 1 to B & 3 to B	174	302

HIGH-VOLTAGE COILS, Y CONNECTIONS

K.v.a.	Connections	Voltage of Secondary Coils, Delta Connection	Voltage of Series-multiple Coils, Y Connection
286	2 to A, 3 to A, 1 to A & 5 to B	57	99
306	2 to A, 4 to A, 1 to A & 5 to B	61	106
335	2 to A, 3 to A, 1 to A & 4 to B	67	116
370	2 to B, 3 to B, 1 to A	74	128
400	2 to A, 4 to A, 1 to A & 3 to B	80	139
445	2 to A, 5 to A, 1 to A & 4 to B	89	154
500	2 to A, 5 to A, 1 to A & 3 to B	100	174

FIG. 18.

The method adopted was as follows: A retort would be heated and then placed on the cold briquet charge, a second retort meanwhile being heated on the heating base; when this second retort had attained a temperature of say 1200° C., the first retort would be lifted from the charge and replaced on the heating base after the second retort was placed on the briquets; this operation was repeated until the charge was at a distilling temperature, namely 950° to 1000° C. The following shows the results of preheating charge 28 in Table 7:

Retort No.	On or Off Charge	Date	Time	Temperature, Degrees C.
1	On	Nov. 6	4 A. M.	520
1	Off	Nov. 6	3:30 P. M.	450
2	On	Nov. 6	3:45 P. M.	730
2	Off	Nov. 7	7:45 A. M.	670
1	On	Nov. 7	8 A. M.	1035

TABLE 7.—*Results Obtained with Preheated Retorts*

Charge Number and Kind of Ore	Weight of Charge, Pounds	Weight of Distilled Charge, Pounds	Per Cent. of Zinc in Charge	Per Cent. of Zinc in Distilled Charge	Weight of Zinc in Charge, Pounds	Kilowatt Intensity	Kw.-hours Consumed	Kw.-hours Consumed per Ton of Ore	Time of Distillation, Hours	Temperature of Top of Retort at Beginning of Distillation, Degrees C.	Temperature at Top of Retort at End of Distillation, Degrees C.	Temperature of Base at Beginning of Distillation [b] Degrees C.	Temperature of Base at End of Distillation, [b] Degrees C.	Weight of Zinc Dust Collected, Pounds	Percentage of Recovery
24. Missouri silicate ore and dross briquets	3110	....	22.11	0.13	687.6	255	2170	2795	8.50	690	....	480	790		
25. Missouri silicate ore	3121	....	19.30	0.83	602.0	237	1300	1665	5.50	860	....	680	900		
26. Missouri silicate ore; some briquets made with old briquets as coke	3097	1759	16.23	Trace	502.0	234	1700	2190[a]	7.25	980	....	780	1415		
27 Missouri silicate ore; some briquets made with old briquets as coke	3022	1634	16.20	Trace	489.5	234	1170	1548[a]	5.00	1035	1460	560	970		
28. Franklinite briquets	3327	....	8.20	0.23	286.0	200	1185	1365	6.00	680	1125	230	400	236.0	82.5
29. Missouri silicate ore	3070	1627	16.45	0.15	505.0	225	1440	1811	6.40	970	1240	140	320	473.8	93.8
30 Missouri silicate ore	3168	1718	17.35	0.11	548.6	152	980	1237	6.50	1290	1310	520	660	523.2	95.1

[a] Overdistilled; unnecessarily high.

[b] Temperature measured in brickwork of base.

These data do not indicate what can be done in preheating, but are given as examples only. The temperatures of first retorts were very much too low to be of much service, but the retorts were used at these temperatures to obtain certain data and because the furnace was not ready to begin distillation until Nov. 7.

By comparing the temperature figures, it will be noted that the radiation from the retort is not rapid. The normal preheating period was 2 to 3 hr., and to obtain the total time of a charge on the base this must be added to the "Time of Distillation" given in Table 7. Under normal rapid and continuous working from base to base on the furnace, the hot retort from a finished charge would be set on a new charge, allowed to remain about 1 hr., and then replaced by a retort at 1300° to 1350° C. from the heating base, and the retort just taken from the charge put on the heating base. After the second retort was on the charge about 1 hr., electrical distillation would be commenced. It need not be especially pointed out that power consumption will be lowest with such rapid and continuous working. Power consumption figures are given in Table 8.

TABLE 8.—*Power Consumption*

Run Number	Kw.-hours per Ton Ore	Per Cent. Zinc Distilled[a] from Charge	Run Number	Kw.-hours per Ton Ore	Per Cent. Zinc Distilled[a] from Charge
1[b]	2540	100.0	16	2200	96.0
2	2270	100.0	17	1645	88.0
3	1540	54.0	18	2120	98.0
4[b]	3260	98.0	19[b]	3200	89.0
5	1645	98.0	20	1760	91.0
6	1720	85.0	21	1720	95.0
7[b]	2540	90.0	22	1920	97.0
8	2240	98.0	23	1760	95.0
9	2180	93.0	24[c]	2795	99.0
10	2420	96.0	25	1665	99.0
11	1760	73.0	26	2190	100.0
12	1600	70.5	27	1548	100.0
13	2700	100.0	28[d]	1365	99.0
14	2460	100.0	29	1811	99.0
15[b]	2620	100.0	30	1237	99.0

[a] Where less than all the zinc is distilled, the operation was purposely stopped to determine relation of extraction and power consumption.

[b] Initial charges. [c] From here on, operation with preheated retorts.

[d] Franklinite charge.

The theoretic power consumption for 60-per cent. zinc ore containing 20 per cent. siliceous residue, made into briquets containing 100 parts ore, 70 parts coke, and 17 parts coke pitch, is 1372 kw.-hr. exclusive of radia-

tion losses. Of this, 421 kw.-hr., the amount required to preheat the charge to 920° C., may be obtained by non-electrical means, as by preheated retorts. The carbon monoxide, which in this large-scale work may be collected, amounts to about 7200 cu. ft. (201 cu. m.) per ton of ore, which at 35 cu. ft. per hp.-hr., is equivalent to 206 hp.-hr., or 154 kw.-hr. The energy in the briquet residue, in cooling from 1200° C. to 25° is equal to 378 kw.-hr. Some of this may perhaps be recovered. The radiation losses can be made very small since, in the nature of the process, the heat energy developed within the charge itself is at once consumed in useful work. The retorts can be heavily insulated. In Table 8, the low power consumption figures with a high degree distillation was obtained under condition of rapid work, and quick transfer of retorts. Continuous steady operation will also materially aid in condensation. All of the work was carried out on exceptionally low-grade ore, giving briquets containing from 16 to 20 per cent. zinc. With higher grade ores, the briquets would contain from 25 to 30 per cent. zinc, but it is not probable that the power consumption would increase proportionately since the time is not necessarily increased and hence radiation losses are kept down.

Zinc Dust Runs.—Runs 28, 29, and 30 were made to produce zinc dust with furnace F. A condenser system consisting of two firebrick boxes, the first directly connecting with the vapor passage, and a 40-ft. (12-m.) train of 30-in. (76-cm.) tile was connected with one base. To immediately cool the vapor at the exit of the vapor passage, an 8-in. (20.3-cm.) iron pipe was passed through the first collecting box directly in front of the vapor passage; air was continually blown through this pipe. The zinc dust was of excellent quality throughout, free from oxide, 97 per cent. passing a 200-mesh screen. The recoveries were very high, as will be noted from Table 8.

Run 28 was made on Franklinite ore, the briquets having the following composition: ore, 100 parts; coke, 85 parts; and pitch 28 parts. The briquets were in excellent condition after distillation and it is very probable that the coke and pitch proportions can be reduced. For the first large run on Franklinite, it was considered undesirable to take any chance on composition.

General Characteristics of Process and Applications.—The furnace and process presents the following characteristics:

1. It maintains the physical and metallurgical conditions of the present-day retort practice, in that it operates with a closed retort within the space of which is maintained a uniform temperature. This produces gas practically free from carbon dioxide, from which the zinc can be condensed as spelter without the formation of blue powder.

2. The energy for the distillation is generated within the charge itself, which fact, combined with proper heat insulation, will give the minimum power consumption possible.

3. It is a large unit furnace, the proposed 12-in. diameter; 72-in. high briquet, 19 per charge, will distil 8½ tons of roasted concentrate per 24 hr., counting on three distillations of 8 hr. each. The handling of material would all be done by crane, as in steel and copper plants. A general design has been worked out, in which the handling of material, the mixing of the briquet charge, the briqueting, the baking of briquets, the charging of retorts, and the discharge of the spent charge is done automatically and mechanically.

4. Probable costs have been calculated, which show a marked reduction over present costs. There will be no pottery and practically no consumption of fireclay. Labor costs will be low. Due to the completeness of distillation the recovery will be higher than in the present-day retort process. The cost of pitch in briqueting is not serious and, with the great increase in byproduct coke ovens, the pitch supply will be plentiful. It has been suggested that the combination of a byproduct plant and the electrical distilling furnace might work out well.

5. The process can be applied to any zinc ore, even to the so-called complex ores.

Acknowledgments

The work described was carried out for Mr. David B. Jones, of Chicago, to whose fertility of suggestion, unfailing courtesy, and faith in ultimate success, the author wishes to make sincere acknowledgment. To Mr. M. F. Chase acknowledgment is made for the most helpful and kindly criticism and suggestions. Mr. Chase was in direct charge of the work at East St. Louis from about the first of June, 1917, the date of the organization of the Metallurgical Laboratories, Inc., the owner of the patents, until January, 1918, when war conditions made it necessary to discontinue the work. The staff organized for the work was made up of Raymond O. Jackson, Thomas M. Bains, Jr., J. Burns Read, and Louis Deitz, Jr., to whose skill and energy much of the success of the work is due and to whom the author wishes to make grateful acknowledgment

DISCUSSION

J. W. Richards, South Bethlehem, Pa.—The illustration of the furnace on p. 189 is almost identical with a furnace I saw in operation in Sweden for making electrodes. Electrodes were placed in the furnace, almost exactly as shown, in a series, and baked in that manner.

Mr. Tucker.—It seems to me that the figures in Table 8, giving the kilowatt-hours per ton of ore, are pretty high.

C. H. Fulton.—Table 8 gives the power consumption. For instance, 1^b, is an initial charge, which means that the charge is heated from the

cold and includes the power to preheat the retort. The power consumption must be taken under normal conditions, as expressed in Nos. 5, 21, or 27. As stated in the abstract of the paper, the power consumption per ton of concentrate normally ranges between 1500 and 1700 kilowatt-hours,

J. W. RICHARDS.—How was the poor conductivity of these briquets overcome in starting the furnace?

C. H. FULTON.—The resistivity of the raw briquet, on account of the hydrocarbons of the pitch, is very high, so that one of the steps of the process is the baking of the briquet at a temperature between 450° and 500° C. At this temperature, the resistance of the briquet is broken down to about 0.6 to 0.7 ohm per cubic inch. There is still a relatively high resistance but the heated retort, which is at a temperature of about 1200° C., is transferred from the previous charge to this charge, and will, within 20 or 30 min., break the resistance of the briquets so that the 175 or 200-volt current will immediately take hold and lower the resistance, as shown in Fig. 5, so that 80 to 90 volts or less will give the proper energy input into the furnace.

J. W. RICHARDS.—In the furnace in Sweden, the raw electrodes were placed in the furnace without any baking. Of course, they were practically non-conductors, so an iron rod about as big as one's finger had been embedded in the middle of each. This was sufficient to start the current flowing. When the current flowed through this rod, it baked the electrode around the rod, and as soon as that part around the rod became baked, the electrode itself became conducting and was gradually heated up from the inside. They thus started with a raw, non-conducting electrode, and the electrode baked itself.

C. H. FULTON.—We conceived the same idea and did considerable experimenting to eliminate the preliminary baking, but found we were unable to make a briquet that would not collapse. The softening of the briquet at certain stages of heating caused the briquets to collapse in the furnace, as explained under the caption Baking the Briquets.

J. W. RICHARDS.—The large amount of heat required to raise these briquets to the temperature and for distilling off the zinc, makes it a wasteful operation. It does not appear to me to be on a competing basis with other furnaces that do not have to remove the heated briquets from the furnace.

C. H. FULTON.—I think perhaps Professor Richards misinterprets the mode of operation, for, in the present-day metallurgy of zinc, the cold charge is put into the retort and the charge is finished and the hot residue is removed. In our process, we not only do the same thing but we do not

allow our retort to cool down, for the hot retort is immediately transferred to a new charge which absorbs the retort heat.

Experiments were under way, to preheat the briquet charge to 500° C. in properly designed ovens, and then place this preheated charge on the base and immediately cover it with the hot retort from a previous charg,e so that the heat of raising the briquets from room temperature to 500° will be saved. Further, it is proposed to take the hot residues from the bases and use the contained heat in suitably designed ovens for baking briquets. As far as I know, there are no metallurgical processes in use at the present time that recover the heat which now goes to waste in residues, such as slags; or in products such as matte, or iron, and the heat in the zinc residues is in the same position as the heat in slags, etc.

J. W. RICHARDS.—I had in mind other electric zinc furnaces in which only the theoretical amount of reducing agent is used, and the energy required to raise excess of reducing agent to the final temperature does not have to be expended in the electric furnace. I had in mind comparison with other zinc electric furnaces, and not with the ordinary retort.

C. H. FULTON.—The amount of energy used in raising the excess coke of the briquet is less than 5 per cent. of the energy used.

Tin Fusible Boiler-plug Manufacture and Testing*

BY L. J. GUREVICH, † B. CH. E., AND J. S. HROMATKO, ‡ B. A., WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

IN the course of the examination, at the Bureau of Standards, of fusible tin boiler plugs for the Steamboat Inspection Service, it became evident that an investigation should be undertaken to determine the precautions necessary in the manufacture of acceptable plugs. The results of the tests of these plugs show that their manufacture has improved, though at present not all of the plugs tested are satisfactory. Table 1 gives the result of tests of some 1500 plugs from about 100 makers. Records of the tests show that several of the makers were able to produce satisfactory plugs with every pouring.

The Steamboat Inspection Service has the following specifications for fusible plugs: "Fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat Inspection Service shall be made of bronze casing with the bore tapering continuously and openly from end to end, and filled from end to end with tin not less than 99.7 per cent. pure and to contain not more than 0.1 per cent. of lead and not more than 0.1 per cent. of zinc. The small end of the bore may be countersunk not more than $\frac{1}{32}$ in. in depth and width, but no recess, thread, or cavity other than this countersink shall be allowed."

TABLE 1.—*Thirty-five-month Testing Record of Fusible Plugs*

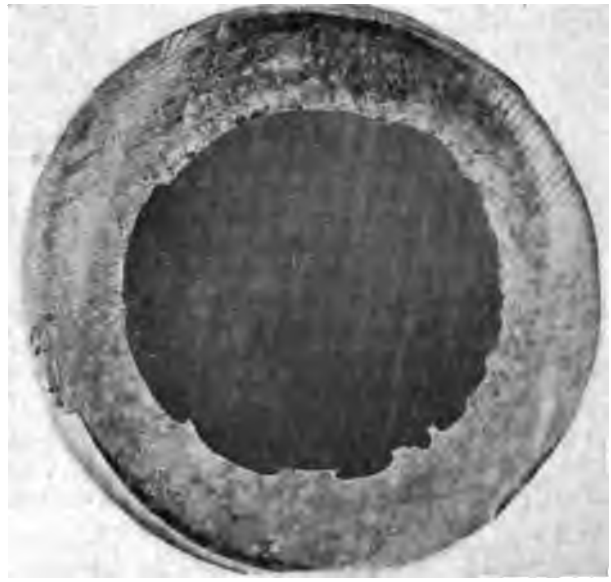
Inspection Period	Number of Fusible Plugs Tested	Passed, Per Cent.	Rejected, Per Cent.	Causes of Rejection: Mechanical Specifications, Per Cent.	Casing not of Bronze, Per Cent.	Melting Point below 230.0° C., Per Cent.	Lead More Than 0.1 Per Cent., Per Cent.	Zinc More Than 0.1 Per Cent., Per Cent.	Copper More Than 0.3 Per Cent., Per Cent.
June-November, 1916	311	52.8	47.2	3.8	11.5	15.1	10.9	1.9	4.5
December, 1916–May, 1917	318	71.4	28.6	2.2	4.4	12.8	5.9	...	2.8
June-November, 1917	228	73.0	27.0	...	9.6	5.2	9.6	...	0.8
December, 1917–May, 1918	214	72.0	28.0	0.9	0.4	11.6	7.0	...	7.9
June-November, 1918	250	70.7	29.3	...	2.0	20.0	5.2	...	2.8
December, 1918–April, 1919	233	78.1	21.9	7.2	1.2	4.7	3.0	...	6.0
Total 35 months	1544	69.7	30.3	2.3	4.8	11.6	6.9	0.3	4.1

* Published by permission of the Director, U. S. Bureau of Standards.

† Assistant Physicist, U. S. Bureau of Standards.

‡ Laboratory Assistant, U. S. Bureau of Standards.

The experimental results show that there are six primary causes for the rejection of fusible plugs. These may be divided roughly into two classes: first, those due to the casing and, second, those due to the purity of the tin filling. Under the first class, rejections are included due to the mechanical and chemical specifications of casing material. The second class includes rejections due to the purity of the tin filling and under this will be discussed the freezing-point determinations of binary tin alloys containing small amounts of copper, lead, zinc, and antimony.



a

FIG. 1.—EFFECT OF OVERHEATING OF TIN AND CASING DURING MANUFACTURE.
a. BRASS CASING FILLED WITH PURE TIN AND KEPT MOLTEN FOR 10 MIN. × 3.

MECHANICAL AND CHEMICAL SPECIFICATIONS

Mechanical Specifications.—The only repeated defect under mechanical specification is the loose filling. This is due to pouring the tin into casings that are below the required temperature.

Casing Material.—Occasionally, plugs that have brass casings are received by the Bureau. This is probably due to the somewhat ambiguous wording of the Steamboat Inspection Service specifications. The exact composition of the bronze to be used is not stated and consequently some of the manufacturers use such alloys as manganese and other bronzes. The brass casing contaminates the tin filling with copper and zinc, the presence of the latter being very detrimental.[1] The nature of the action

[1] Burgess and Merica: Bureau of Standards *Tech. Paper* 53; also in *Trans.* Amer. Inst. Metals (1915) **9**, 21.

b

FIG. 1.—(*Cont.*). *b*. BRASS CASING AS RECEIVED FROM MAKERS SHOWING JUNCTION OF BRASS CASING AND TIN FILLING. × 150.

c

FIG. 1 —(*Cont.*). *c*. JUNCTION OF BRASS CASING AND TIN FILLING; THE FILLING HAVING BEEN KEPT MOLTEN IN THE CASING FOR 5 MIN. × 500.

between the molten tin and the casing is shown, in Fig. 1, to be a simple solution of the casing material by the molten tin. Copper and zinc are introduced from the brass casing while only copper, the less objectionable impurity of the two, is introduced from the bronze casing.

In order to determine the best casing material and at the same time determine the lowest temperature for pouring and preheating the casings, a series of experimental fusible plugs were made up and tested. Two different alloys were used for casings. They were 88Cu, 10Sn, 2Zn (Series G) and 87Cu, 7Sn, 5Zn, 1Pb (Series M). Two series of eight each were made. The casings were 1¼ in. (31.8 mm.) round, ⅝ in. (15.8 mm.) bore, and ¾ in. (19 mm.) high. Four of each series were filled using no flux, while the rest were filled using zinc chloride as a flux. The tin was poured at about 250° C., while the temperature of the casings is shown in Table 2. The tin was then melted out into an iron mold and analyzed for impurities introduced.

Two other series of ten each, using the same casing alloys, were then prepared. All the casings were first tinned by immersion in pure tin, using a zinc-chloride flux. A good smooth tinned inner surface resulted with the tinning bath between 250° and 260° C. The temperatures for preheating the casings and pouring of tin to produce tight fillings has been found to be from 250° to 275° C. The tin-pouring temperature and the temperature of preheated casings, together with the chemical analysis of the melted out tin are given in Table 3.

TABLE 2.—*Effect of Preheating Temperature, and also of Zinc-chloride Flux on Contamination of Tin Filling*

Temperature of Preheated Casings, Degrees C.	Time for Tin to Solidify[a]	Series GF & MF Using $ZnCl_2$ Flux	Chemical Composition of Tin Filling			Series G & M Using No Flux[b]	Chemical Composition of Tin Filling		
			Copper, Per Cent.	Lead, Per Cent.	Zinc, Per Cent.		Copper, Per Cent.	Lead, Per Cent.	Zinc, Per Cent.
To 150...	20.0 sec.	G4F[c]	0.04	.....	0.13	G4	0.04	.....	trace
To 230...	3.5 min.	G5F	0.12	.....	0.26	G5	0.09	.....	0.04
To 300...	7.5 min.	G6F	0.17	.....	0.24	G6	0.22	.....	trace
To 400...	7.0 min.	G7F	0.07	.....	0.13	G7	1.03	.....	0.04
To 150...	20.0 sec.	M1F[c]	0.08	0.08	0.17	M1	0.02	0.05	0.08
To 230...	3.5 min.	M2F	0.09	0.08	0.17	M2	0.05	0.07	0.09
To 300...	7.5 min.	M3F	0.08	0.12	0.20	M3	0.12	0.07	0.23
To 400...	7.0 min.	M4F	0.08	0.07	0.12	M4	0.07	0.07	0.13

[a] Tin used contained: Lead, 0.06 per cent.; zinc less than 0.04 per cent.; iron, less than 0.03 per cent.

[b] All fillings were found to be loose. On melting out only M4 and G7 were well tinned on the inside.

[c] Loose fillings.

Purity of Tin Filling

The impurities of the tin fillings may be divided into two classes: those present in the original tin; and those introduced during the manufacture of the plug. By choosing proper pig tin, the first class is easily eliminated. The second depends entirely on the care and attention given to the manufacture of plugs by the maker. Unserviceable plugs result from undue overheating of either the casing or the tin, or both during pouring, and from carelessness in using dirty pots previously used for melting solder, lead, or zinc. Table 4 indicates how easily as much as 15 per cent. of copper may be introduced into the filling.

Table 3.—*Effect of Pouring and Preheating Temperatures on Contamination of Tin Filling*

Casing	Temperature of Casing, Degrees C.	Temperature of Tin, Degrees, C.[a]	Time to Solidify	Chemical Composition of Tin Filling			Tightness of Filling
				Cu, Per Cent.	Pb, Per Cent.	Zn, Per Cent.	
M12	150	240	20 sec.	Not analyzed			Loose
M13	200	240	1 min. 15 sec.	0.12	.....	0.02	Slightly loose
M14	250	240	2 min. 40 sec.	0.13	.....	0.03	Tight
M5	Room	260	5 sec.	Not analyzed			Loose
M6	150	260	30 sec.	0.007	0.04	0.06	Tight
M7	250	260	2 min. 40 sec.	0.13	0.01	0.03	Tight
M8	Room	300	5 sec.	Not analyzed			Loose
M9	150	300	40 sec.	Not analyzed			Loose
M10	200	300	1 min.	0.04	.....	0.02	Tight
M11	250	300	2 min. 30 sec.	0.11	.....	0.03	Tight
G15	150	240	20 sec.	Not analyzed			Loose
G16	200	240	1 min. 15 sec.	0.14	.....	0.02	Tight
G17	250	240	2 min. 40 sec.	0.14	.....	0.02	Tight
G8	Room	260	5 sec.	Not analyzed			Loose
G9	150	260	30 sec.	Not analyzed			Loose
G10	250	260	2 min. 40 sec.	0.15	.....	0.01	Tight
G11	Room	300	5 sec.	Not analyzed			Loose
G12	150	300	40 sec.	Not analyzed			Loose
G13	200	300	1 min.	0.05	.....	0.02	Tight
G14	250	300	2 min. 30 sec.	0.07	.....	0.02	Tight

[a] Tin used contained: Cu, less than 0.01 per cent.; Pb, less than 0.01 per cent.; Zn, not detected.

TABLE 4.—*Solution of Zinc and Copper by Molten Tin from Casing*

Casing	Time of Heating	Zinc in Tin	
		Before Heating, Per Cent.	After Heating, Per Cent.
1. 60Cu-40Zn brass....	Plug poured in ordinary way and then kept molten for 10 min. with Bunsen burner.	....	1.45
2. 60Cu-40Zn brass....	Plug as received and melted out.	0.21	
60Cu-40Zn brass....	Plug from same company and from same heat, kept molten for 10 min.	....	1.31
3 88Cu-10Sn-2Zn bronze.....	Plug poured in ordinary way and then kept in molten condition as No. 1.	Cu 0 Zn 0	Cu 4.3 Zn 0.06
4. 90Cu-10Sn bronze...	Plug poured and kept in molten condition for 1 min.	....	Cu 0.96
90Cu-10Sn bronze...	Plug poured and kept in molten condition for 5 min.	....	9.21
90Cu-10Sn bronze...	Plug poured and kept in molten condition for 10 min.	....	15.21

TABLE 5.—*Freezing Points and Chemical Analyses of Tin from Few Rejected Fusible Plugs*

Plug No.	Melting Point, Degrees C.	Chemical Analysis		
		Copper, Per Cent.	Lead, Per Cent.	Iron, Per Cent.
2635	229.1	0.16	1.04	0.02
2636	228.9	0.10	1.05	0.02
2650	229.4	0.12	0.79	0.02
2651	228.7	0.15	0.73	0.01
2656	228.5	0.22	0.91	0.02
2658	228.7	0.20	0.90	0.02
2788	228.5	0.50	0.01	0.10
2790	227.5	0.40	0.39	<0.06
2837	226.8	0.78	0.11	<0.03
2849	229.4	Cu & Bi 0.80	0.43	<0.03
2866	228.9	0.57	0.15	<0.04
2887	224.7	0.66	1.54	<0.08
2888	229.6	Cu & Bi 0.54	0.58	<0.03
2972	227.1	0.80	0.22	<0.03
2985	228.1	0.65	0.10	<0.03

A somewhat quick method for determining the purity of tin is the determination of its freezing point[2] which detects such small amounts of impurities as 0.1 or 0.2 per cent. This method has been checked by

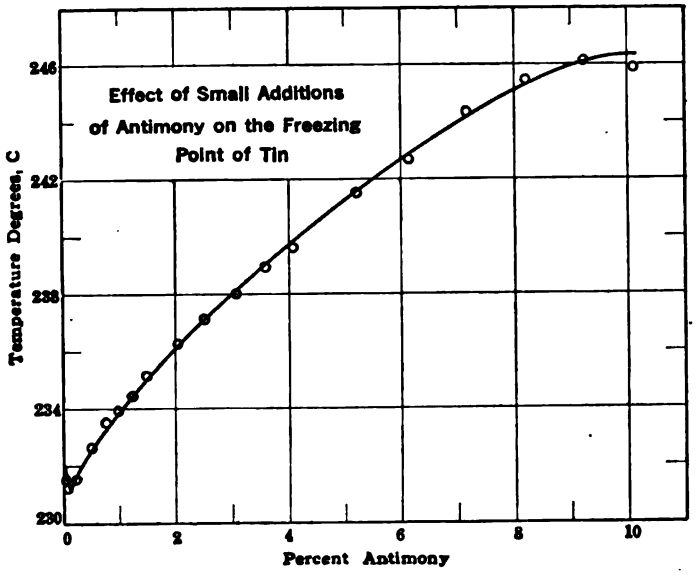


FIG. 2.—FREEZING-POINT CURVE OF ANTIMONY-TIN ALLOYS.

numerous chemical analyses and Table 5 shows that a freezing point below 230° C. always indicates an excess of impurities. However, it has been found that a freezing point above 230° C. does not always insure the purity of the tin.

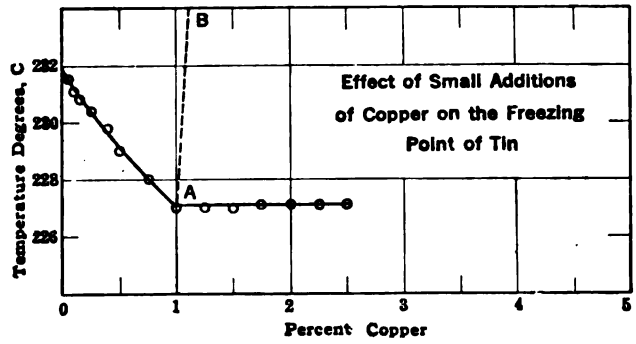


FIG. 3.—FREEZING-POINT CURVE OF COPPER-TIN ALLOYS.

Freezing-point Determination.—In order to determine to what extent the freezing point of tin is influenced by small amounts of such impurities

[2] Burgess and Merica: *loc. cit*

as copper, zinc, lead, and antimony, a series of binary alloys of tin were made, containing from 0.05 to 4 per cent of the above metals.

The metals used were of the following degree of purity: (*a*) The

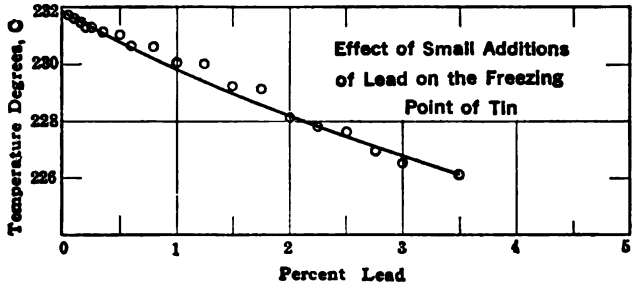


FIG. 4.—FREEZING-POINT CURVE OF LEAD-TIN ALLOYS.

tin contained less than 0.02 per cent. of total impurities, having a melting point of 231.9° C. (*b*) The alloying metals were electrolytic shot copper, B. S. standard melting point zinc, Baker's silver-free test lead, and Kahlbaum's antimony.

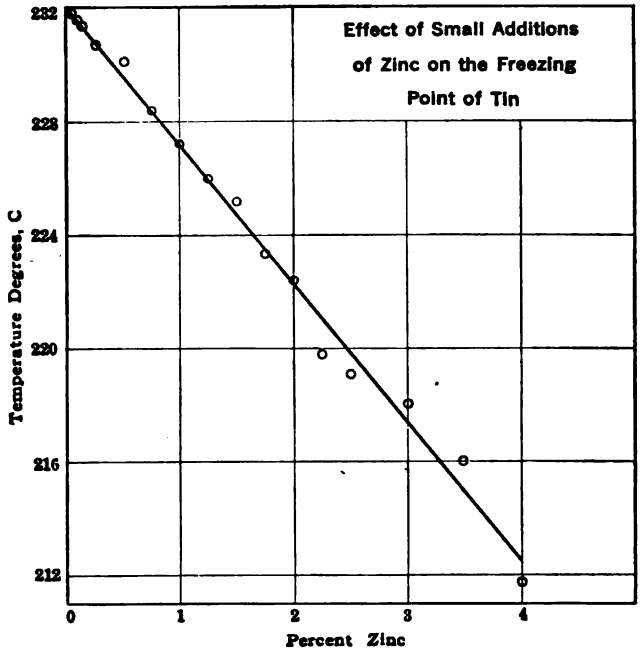


FIG. 5.—FREEZING-POINT CURVE OF ZINC-TIN ALLOYS.

Samples of 20 gm., with the exception of the antimony series, were heated in an electric furnace above their freezing points. Then the freezing point was determined by an inverse-rate cooling curve taken

with a Leeds & Northrup precision potentiometer and a base thermocouple of No. 32 gage copper and No. 30 gage constantan wire. The couple was protected by a 3-mm. glass tube, inserted into the alloy contained in a 12-mm. bore glass tube. The antimony alloys were heated in a solder bath by a gas flame, but the freezing point was detected in the same manner. The results of the freezing-point determinations on the various alloys are shown graphically in Figs. 2, 3, 4, and 5. The lowering of the freezing point of tin by small amounts of antimony, Fig. 2, is of interest as available information on the subject indicates an immediate rise of the freezing point[3] on the first addition of antimony.

Copper lowers the freezing point until the alloy contains 1 per cent., then a sharp rise takes place as indicated, in Fig. 3, by the dotted line *AB*. The determination of this line proved to be rather difficult on account of the extremely slow cooling necessary to affect the complete transformations which take 2 and 3 hr.[4] The eutectic transformation occurred at 227.1° C. and was easily detected.

The freezing-point curves of lead-tin and zinc-tin alloys are practically straight lines, the depression of the former for 1 per cent. of lead being about 1.7° while 1 per cent. zinc depresses the freezing about 4.9° C. This rather small depression of the freezing point by a considerable amount of lead explains the erratic behavior of the melting-point test for the determination of tin purity. The question of the effect produced by the combination of two or more of the impurities is under investigation at present and the results should be available very soon.

Conclusions

From the foregoing results, the following conclusions have been reached as to the precautions to be taken in the manufacture of fusible plugs:

1. The pig tin should be at least 99.7 per cent. pure, containing not more than 0.1 per cent. lead, or 0.1 per cent. zinc, which are the requirements of the Steamboat Inspection Service.

2. The casing should be of bronze, an alloy the major constituents of which are copper and tin. Small amounts of zinc and lead increase the ease of casting and machining and are not objectionable if not present in greater amounts than in the following compositions:

	I	II
Copper	88	87
Tin	10	7
Zinc	2	5
Lead	..	1

[3] Heycock and Neville: *Jnl.* Chem. Soc. (1890) **57**, 376.
R. W. Williams: *Zeit. Anorg. Chem.* (1907) **55**.

[4] Heycock and Neville: *Phil. Trans.* Roy. Soc. London (1904) **202A**, 19.

3. The pot or crucible for melting the tin should not be used for melting other metals, thus doing away with the liability of contaminating the good tin when these are not thoroughly cleansed.

4. Casings should be tinned on the inside by the same grade tin as is used for filling, but the tin left over from this process should not be added to the filling to be used. Zinc-chloride flux may be used although hydrochloric acid is preferred, though no flux need be used during the filling process.

5. The casing should be preheated to not above 250°–275° C. (482°–527° F.) and tin should be poured at a temperature not above 275°–300° C. (527°–572° F.).

The authors wish to express their appreciation of the helpful suggestions of Dr. G. K. Burgess, under whose direction the work was carried out.

DISCUSSION

WM. A. COWAN, Brooklyn, N. Y. (written discussion).—This is evidently an excellent continuation of the work described in the article "An Investigation of Fusible Tin Boiler Plugs" by Messrs. Burgess and Merica.[5] The present paper gives information of much value in connection with the manufacture and inspection of fusible boiler plugs, and the investigation of the cooling curves of tin with various other metals close to the tin side of the diagram is very interesting. These curves corroborate in all cases, except that of antimony, the diagrams given by other investigators. However, only the liquidus curves of the thermal equilibrium diagrams are given, except for copper-tin alloys where one branch only of the solidus (representing the freezing of the eutectic) is given, the corresponding branch of the liquidus curve being represented by a dotted line. These are referred to in all cases as the freezing-point curves, or, as in Table 5, as the melting points. It might be clearer if they were referred to as the liquidus curves, representing only the initial freezing points of the alloys; and it would add to the value of the investigation if the cooling of the large number of alloys examined had been carried down to a lower transformation point. This would give the solidus curve and would show just how close to pure tin the eutectics are found, or would show the saturation points in case solid solutions are formed.

The determination of these additional points, particularly in cases where an eutectic is formed, should give more certain information as to the purity of the tin and as to its actual melting point or temperature of probable failure in fusible boiler plugs. For instance, in the case of tin from plug number 2788 in Table 5, which contains 0.50 per cent. copper,

[5] Bureau of Standards *Tech. Paper* 53; also in *Trans.* Amer. Inst. Metals (1915) 9, 21.

this alloy, disregarding the presence of iron, would be composed of 50 per cent. eutectic mixture containing 1 per cent. of copper and 50 per cent. excess tin. In cooling, the excess tin would begin to freeze out at about 228.5° C. and continue freezing through the range of temperature from 228.5° to 227.1°. The balance of the metal consisting of eutectic mixture would then freeze out at the latter temperature. The actual melting point under the conditions of use, or the temperature at which a fusible boiler plug filled with this alloy would blow out, would be at some temperature between these points, probably very close to 227.1° C., rather than at 228.5°, which is given as the melting point in the table.

In the case of the addition of antimony to tin it is interesting to note that a slight depression in the freezing point is shown by the authors to be caused by 0.10 per cent. of antimony. As described, this has not been noted heretofore in the equilibrium diagram of this series of alloys. The statement is evidently founded on the determination of only three alloys and it would be interesting if the authors would report additional tests corroborating this, eliminating the possibility that the slight depression in the freezing point may have been caused by the presence of a slight amount of a third element. The depression would undoubtedly be caused by the presence of an eutectic (if such exists) of the composition represented by the lowest temperature point, namely, 0.10 per cent. antimony and 99.90 per cent. tin, or else by a ternary eutectic formed with another element present as an impurity. If present, the eutectic should have shown in the cooling curves of the alloys located on each side of the alloy of the lowest melting point.

ALLEN P. FORD,* Bridgeport, Conn. (written discussion).—The specification of 99.7 per cent. pure for the pig tin is very lenient. As a matter of fact, Banca tin will run very much better than this; and it is well that it does so, because if pig tin no better than 99.7 per cent. was used, it would be very difficult to keep within the limits in the final result. We have no trouble in getting pig tin running 99.9 per cent. or better; and if this tin is properly handled, there is no difficulty in the final result.

The conclusion in regard to the analysis of the casing is, in the main, correct. This company uses a red brass, or bronze, similar to the analysis given under II, except that our lead runs a little higher. I do not think, however, that this affects the results, because where we have had any trouble, it has always been with the copper; and this agrees with the statement in the paper at the top of p. 230 to the effect that "while copper and zinc are introduced from a brass casing, only copper is introduced from a bronze casing."

In the matter of temperature, we do not quite agree with the results given in the paper. At the temperature given, we have found it very

*Metallurgist, Crane Co.

difficult to make the tin filling stick in the casing. We have found that the tin can be poured considerably above the given temperature, that is, 275° to 300° C., and at the same time have it set in much less than ½ min. We find that the time of setting is a very good rough guide as to what the result will be. If the tin is what it should be in the first place and is poured at a temperature that will allow it to set in about 20 sec. or less, rarely or never will trouble be experienced; but if the time of setting goes much over this time, there is likely to be trouble; and if it goes to 1 or 2 min., the molten metal is almost certain to pick up enough metals from the casings to cause the plugs to be rejected.

One thing further to show how little a thing will affect the result. On one occasion we got a copper result in one of the tin fillings that, although not above the limit, was higher than it should have been. Investigation showed that this had been melted out by a man who did not understand the work; further investigation showed that the result could be affected by the manner in which this filling was melted out. To demonstrate it, two plugs were poured as follows: The two casings were placed upon the heating surface side by side, so that there could be no material difference in their temperature. A small ladle of tin holding just enough for three or four plugs was dipped out of the crucible of melted tin and these two casings filled, pouring one immediately after the other from the same small portion of melted tin. The two plugs were then sent to the laboratory. One of them was placed on a tripod over a small porcelain receptacle, with the large end of the tin filling down, and then gently heated with a Bunsen burner all around it until the tin filling dropped out. The other plug was placed on a similar tripod, but with the small end of the filling down, and then heated strongly on one side with a hot flame until this filling melted out. These two fillings were then separately melted and the buttons analyzed; 0.075 per cent. copper was found in the first and 0.122 per cent. in the second.

This simply shows how sensitive fusible plugs are to influences of this kind, and how expert and careful one must be in handling them to avoid error. We have even a little evidence that the copper in the tin filling may be perceptibly increased by threading the casing (which is done after the plug is filled) with a dull tool, which would necessarily heat the casing somewhat. Determinations have been made that show a slight increase apparently due to this cause; but in this case there were other possible causes present and it was not positively proved.

Manufacture and Electrical Properties of Constantan

BY F. E. BASH,* CH. E., PHILADELPHIA, PA.

(Philadelphia Meeting, September, 1919)

CONSTANTAN is an alloy of copper and nickel that is extensively used, under a number of trade names, as a resistance wire with a low temperature coefficient of resistance, and one of the elements of base-metal thermocouples, iron usually being the other thermoelement, although for low-temperature work copper is also used. Before the war, constantan was imported, in common with many other technical necessities. Since it required considerable time to receive the constantan after it was ordered, fairly large stocks were kept on hand; but after the beginning of the war no more was imported and the stocks of foreign material were exhausted about the same time that the steel and munition manufacturers began to need great quantities of it for thermocouples for the heat treatment of steel.

To meet this demand, the International Nickel Co. began manufacturing constantan that met all the requirements of the users of resistance wire but did not give the same electromotive force against iron as the German material and consequently could not be used with instruments calibrated for a definite e.m.f.-temperature relation. It so happened that all the constantan made had an e.m.f. lower than that necessary to meet the specifications of the Leeds & Northrup Co. for whom this investigation was carried out. If some had been higher and some lower, good wire could have been obtained by a process of selection, but as it was no wire at all could be procured. To remedy this situation, a thorough investigation was started with the close coöperation of the International Nickel Co. and the Electrical Alloys Co.

The specifications to which the constantan had to conform were that it should give an e.m.f. of 47.40 millivolts against pure iron at 1500° F. (816° C.) with the cold-junction temperature at 0° F., or a proportional e.m.f. at temperatures near 1500° F. The method of checking a wire was as follows: It was first welded to a piece of iron wire; Armco iron was found to be satisfactory but iron with greater than 0.1 per cent. carbon would give a lower e.m.f. against the same piece of constantan than pure iron. The couple was then insulated and the fire end was tied to the

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porcelain protecting tube of a platinum-platinum + 10 per cent. rhodium thermocouple and the two put in a checking furnace.

The checking furnace was of the vertical wire resistor tube type, the interior dimensions being 7 in. (17.7 cm.) in diameter by 12 in. deep with a small sil-o-cel block in the center to rest the couples upon. The furnace was practically uniform in temperature throughout, so that it was assured that the two couples would come to the same temperature. To the ends of the iron-constantan couple wires were attached leads of like materials which carried the cold junction to the portable potentiometer, which had an automatic cold junction compensator. The e.m.f. generated by the couple was read by the potentiometer and the temperature of the hot junction was obtained by reading the platinum thermocouple with another potentiometer, the two being so arranged that one operator quickly read both.

Another and quicker method of checking, sometimes employed, consisted of having a number of base-metal couples made up which were checked at frequent intervals so that the amount that the constantan varied from the standard curve was always known. The piece to be tested was tied with a number of wrappings of iron wire to the checking couple at the hot junction after which the couple and sample were put in the furnace. After they had come to temperature, the checking couple was read and then the lead attached to the constantan wire of the couple was transferred to the sample and the e.m.f. between the sample and the iron read. In this manner the sample could be checked against the known piece of constantan, by comparing the two readings that gave the e.m.f. of the known and unknown constantan against the same piece of iron.

The method of wrapping the wire around the sample and couple to make electrical connections was proved to be free from error, as a measurement was made in that manner and another was made after the thermocouple and sample had been welded together; both gave the same results.

The checks are stated as so many degrees plus or minus or so many millivolts plus or minus, which means that the sample is that far above or below the standard e.m.f. at 1500° F. For instance, −10° F. (−5.6° C.) or −0.35 millivolts would mean that the constantan tested gave an e.m.f. of 47.05 millivolts at 1500° F. (816° C.) instead of 47.40; 47.05 being the standard e.m.f. for 1490° F. (810° C.).

When it was first noted that constantan with the proper e.m.f. could not be obtained, a number of samples were checked and afterward analyzed. It was found that two wires might give the same check but have different analyses, so the question of effect of working and annealing was taken up. A complete analysis of one sample of constantan follows:

COMPOSITION OF CONSTANTAN

ELEMENT	PER CENT., BY WEIGHT
Copper	54.15
Nickel	43.70
Iron	0.435
Manganese	1.34
Cobalt	0.16
Chromium	0.033
Sulfur	0.0237
Phosphorus	0.0010
Silicon	0.098
Carbon	0.14
Total	100.0807

Before annealing tests were started, it was desirable to know how uniform in composition the wire ran and also how homogeneous an ingot was as cast. To test the ingot, one, 4 by 4 by 40 in., was selected from a melt of which the heat analysis was as follows: copper, 53.72 per cent.; nickel, 44.83 per cent.; iron, 0.41 per cent.; sulfur, 0.018 per cent.; silicon, 0.04 per cent.; carbon, 0.04 per cent.; manganese, 0.93 per cent. The ingot was then sawed in the middle and also about 3 in. (7 cm.) from each end. These pieces were then sampled by drilling at the center, in the corners, and halfway between the center and the corner. Sample No. 1 represents the two opposite corners; No. 3 is a sample from the middle, and No. 2 is a sample halfway between Nos. 1 and 3. The analyses of these samples were as follows:

	BOTTOM NO. 1, PER CENT.	BOTTOM NO. 2, PER CENT.	BOTTOM NO. 3, PER CENT.
Copper	53.63	53.58	53.55
Nickel	44.94	45.00	45.00
Iron	0.36	0.35	0.36
Sulfur	0.019	0.021	0.022
Silicon	0.04	0.05	0.05
Carbon	0.03	0.036	0.04
Manganese	0.96	0.95	0.96

	MIDDLE NO. 1, PER CENT.	MIDDLE NO. 2, PER CENT.	MIDDLE NO. 3, PER CENT.
Copper	53.75	53.55	53.73
Nickel	44.84	44.99	44.80
Iron	0.36	0.35	0.35
Sulfur	0.017	0.016	0.020
Silicon	0.05	0.05	0.05
Carbon	0.04	0.04	0.04
Manganese	0.93	0.99	0.99

	Top No. 1, Per Cent.	Top No. 2, Per Cent.	Top No. 3, Per Cent.
Copper	53.66	53.67	53.77
Nickel	44.90	44.88	44.83
Iron	0.35	0.36	0.37
Sulfur	0.017	0.016	0.016
Silicon	0.05	0.05	0.04
Carbon	0.03	0.04	0.036
Manganese	0.97	0.97	0.93

These analyses proved conclusively that the ingot was homogeneous throughout and later analyses on a single coil of wire drawn from such ingot proved it also was homogeneous in composition.

To determine the effect of annealing, a No. 8 B. & S. gage wire was checked as received from the wire manufacturer in an annealed state, it was then suspended in a long annealing furnace built for the purpose, so that any desired atmosphere could be maintained by passing a gas through it. The sample would be annealed for different lengths of time at different temperatures, and after each operation it was rechecked.

The results of this investigation showed that the annealing did not change the e.m.f. against iron. Oxidizing, neutral, and reducing atmospheres and temperatures from 1500° F. (816° C.) to 1750° F. (954° C.) were all tried with the same result. The only condition that affects the e.m.f. is a very uneven anneal with one end say at 600° F. and the other at 1500° F.; this may give a considerable error.

To determine the effect of working, a wire was annealed, tested, and drawn through a die until it was hard; it was then reannealed and tested. No errors outside of possible experimental errors of reading and manipulation were found. The wire was then redrawn, reannealed, and tested with the same result as before. With the assurance of no appreciable error from working and annealing, the problem was attacked from the standpoint of composition.

The next point to determine was the relation between pure copper-nickel composition and e.m.f. against iron. This was done by making a number of melts in a vacuum furnace in alundum crucibles from electrolytic copper and nickel and determining their e.m.f. against iron. Part of this work was done by Prof. M. A. Hunter, of Rensselaer Polytechnic Institute, and a number of samples were obtained from Dr. John F. Thompson of the International Nickel Co. The information obtained was put in the form of a curve, which is reproduced in Fig. 1. From this it will be seen that copper gives a low e.m.f. against iron but that addition of a small amount of nickel causes it to reverse its sign with respect to iron and to rapidly increase in value to a maximum at about 60–40 copper-nickel and then drop slowly with increase of nickel to about 25 millivolts for pure nickel. From the curve it is apparent that the most

logical composition to select for thermocouple use would be around the peak so that a small variation in copper or nickel content would not materially affect its e.m.f., and because it is desirable to have as large an e.m.f. as possible for the thermocouple. The composition selected for experimentation was 55–45 copper-nickel.

The next step was to determine the effect of impurities on the pure alloy. It was expected that the various impurities would lower the e.m.f., as standard constantan with approximately 55–45 copper-nickel ratio, only gives an e.m.f. of 47.40 millivolts while the pure alloy gives 53.25 millivolts at 1500° F. The largest constituent of constantan after copper

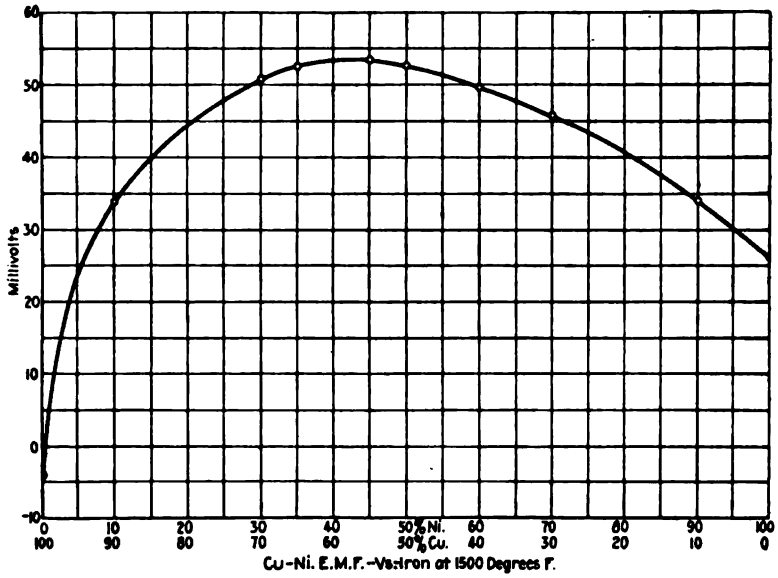


FIG. 1.—RELATION BETWEEN PURE COPPER-NICKEL COMPOSITION AND E.M.F. AGAINST IRON.

and nickel is manganese, which is added to increase the working properties, so its effect was the first investigated. A number of melts were made in a vacuum furnace. Later, in a carbon-resistor furnace, a large number of melts were made, in which all the impurities were varied and combined.

The furnace was of the granulated carbon resistor type with a capacity of 7.5 kw. In the center of the resistor was placed a No. 1 Dixon graphite crucible with the bottom sawed off so that only a cylinder remained to hold back the granulated carbon. In the bottom of this cylinder was placed a thin layer of granulated carborundum, as it did not seem to interact with the alundum crucibles at the high temperatures in the same manner as the carbon.

In this prepared well was placed the small alundum or other crucible containing from 50 to 100 gm. of metal charge, and a lid that fitted the

graphite crucible and completely enclosed the metal containing crucible was placed on top. This lid had a ¼-in. (6.35 mm.) hole in it for purposes of observation and small additions. The furnace top was covered with a ceramic lid, which kept the resistor from cooling off rapidly; this also had a hole through it in line with the hole in the crucible lid. This assured a reducing atmosphere in the furnace.

The effect of crucibles was tried by making a number of melts of the same composition in crucibles of different material. Clay-graphite, clay, sand, alundum and silica were tried with results as follows:

Clay-graphite put so much silicon into the metal that it was almost impossible to roll it. It was, therefore, impossible to use it with the assurance that the final alloy would not contain anything other than that which was actually intended.

Clay did not stand up satisfactorily in the furnace.

Sand crucibles were fairly satisfactory but did not stand the furnace conditions very well.

Alundum crucibles were very satisfactory from every standpoint, except that most of them only stood one heat, as they usually cracked on cooling or on the second heating, so that they proved expensive. They also interacted with the walls of the graphite cylinder in the furnace if they touched at any point and a number of heats were lost due to the side of the crucible being eaten away in this manner. Since they did not contaminate the metal, however, and stood the high temperature, they were used in most of the melts.

One quartz crucible was tried; this proved satisfactory for a number of melts.

To make a melt, the nickel was weighed in the form of small pieces sheared from a slab of the electrolytic material. The copper was also electrolytic in the form of small strips cut from sheets. These two metals were charged with the nickel at the bottom and the whole melted down. Great care was exercised to keep the alloy in a reduced condition as 0.35 per cent. of oxygen forms a eutectic with copper and it was found that if a sample was allowed to be oxidized slightly while melting the e.m.f. of the resulting alloy was greatly affected. In heating, the copper generally oxidized on the surface from the air in the furnace and this formed a thin scum or slag on top of the liquid metal. This was reduced by a few grains of carbon dropped in, just enough being added to unite with the oxide. The metal was thoroughly stirred with a small silica tube and then cast in an iron mold, which had a cross-section of approximately ¼ in. (6.3 mm.) square. This small ingot was put through a pair of hand rolls and reduced to a wire about 0.1 in. (2.5 mm.) square, after which it was annealed in an electric furnace and tested for e.m.f. The analysis of the manganese, nickel, and ferrosilicon used is as follows;

Goldschmidt Manganese		Electrolytic Nickel		Ferrosilicon	
Element	Per Cent.	Element	Per Cent.	Element	Per Cent., Approximate
Manganese.....	95.30	Nickel.....	99.80	Silicon.....	70.00
Iron.....	2.86	Iron.....	0.10	Iron.....	30.00
Carbon.....	0.16				
Sulfur.....	0.062	Total.....	99.90	Total.....	100.00
Silicon.....	1.38				
Aluminum.....	0.18				
Total.....	99.942				

Manganese was added in different proportions up to 2 per cent. for a ratio of copper-nickel of 55–45. The 100-gm. samples were made up with 55 gm. of copper and 45 gm. of nickel and varying amounts of manganese. The final results, in the form of a curve, are shown in Fig. 2. The points obtained fell very well on the line but all varied somewhat from those

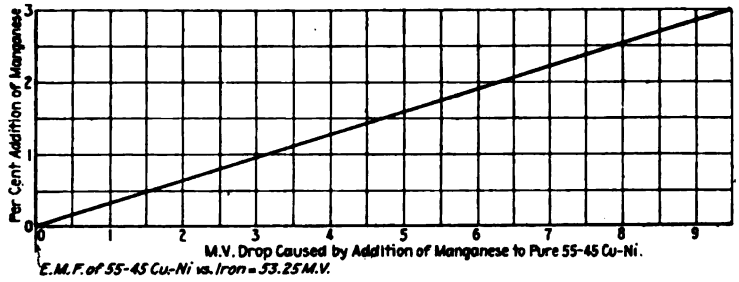


Fig. 2.—Effect of manganese on e.m.f. of 55-45 Cu-Ni against iron.

obtained from melts in the vacuum furnace; the effect of the manganese additions in the case of the vacuum furnace was somewhat greater. The values for the melts in the resistor furnace were used in the calculations, however, as being probably nearer to actual industrial conditions.

The next impurity tried was iron. It was found to have about twice as much effect as manganese so that this element had to be very carefully controlled in making melts. The curve showing its effect on 55–45 copper-nickel is given in Fig. 3.

The effect of silicon was found by adding ferrosilicon of known composition to the copper-nickel and then subtracting the known effect of the iron. This method was not very satisfactory but was the best that could be done at the time as pure silicon was not available. It appears that silicon has an effect almost as great as iron. It was added in as large quantities as it was possible to still get a metal that was workable; 0.3 per cent. was the greatest addition. The curve for silicon is shown in Fig. 3.

To determine the effect of carbon, a melt of pure copper-nickel was made and a small quantity of carbon particles stirred in; shortly after-

ward the metal was poured. The resulting alloy was analyzed for carbon and a check made for the electrical effect. A melt made in a graphite crucible was analyzed for carbon but the point determined fell off the curve obtained by the other method. This was probably due to silicon being present although it was not analyzed for. The effect of carbon is also shown in Fig. 3.

No other elements were tested out. Cobalt was not considered as likely to affect the e.m.f. strongly, as it is so near to nickel in its properties and it does not seem to have much effect, from all the data obtained on the other elements.

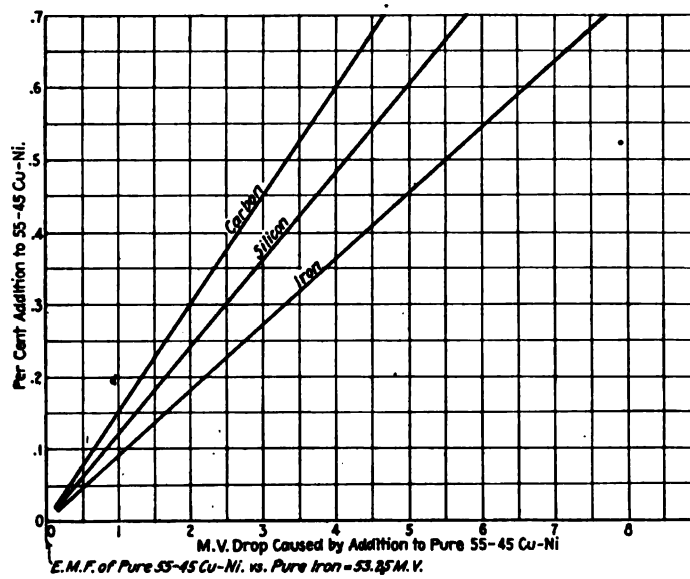


FIG. 3.—EFFECT OF CARBON, SILICON, AND IRON ON THE E.M.F. OF 55-45 CU-NI AGAINST IRON.

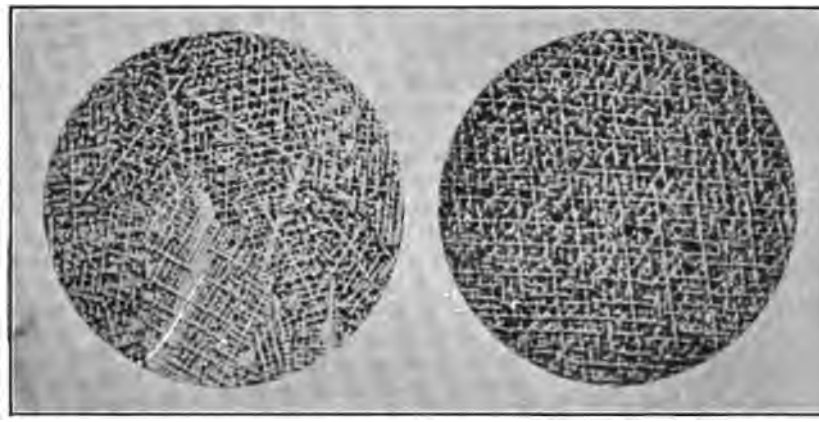
The effect of combinations of the above impurities was tried with varying success. Fifteen melts were made up with different combinations of iron and manganese to determine if their properties were additive. Sometimes the result would check the calculated value and sometimes not. It is probable that the manganese acted somewhat as a scavenger on the oxygen and was thus accounted for. Silicon, iron, and manganese were also tried with about as good results as with the iron and manganese.

During the laboratory experimentation, the International Nickel Co. was doing everything possible to make a satisfactory melt, and its heat analyses were carefully compared with the results of tests on the finished wire. In some cases, the calculated e.m.f. would almost check exactly the value obtained on the sample and in other cases the calculated e.m.f.

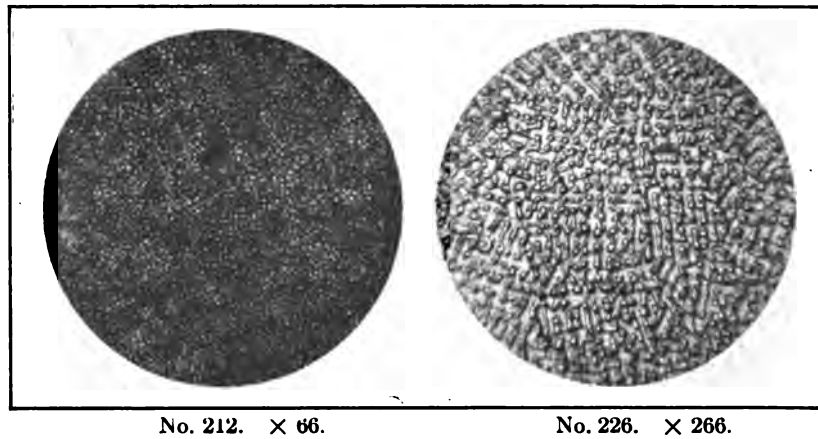
was lower than the actual and occasionally higher, although not so often as lower. This may be accounted for, to a certain extent, by the fact that the heat analysis was obtained by sampling a number of ingots poured from probably three ladles and the sample tested for electromotive force was from one ladle. Since additions are made to each ladle and not all the added material goes into the metal, it is reasonable to suppose that the heat analysis might be different from that of the sample tested. It is also possible that all the impurities may not always be active, as the manganese may combine with oxygen or sulfur. This would account for the calculated e.m.f. being lower than the actual. Slight errors in analysis would also account for errors.

A few examples of the calculation follow. The method used in mak-

No.	Composition		Composition for Cu+Ni = 100 Per Cent.	Partial E.m.f., Millivolts		Total Calculated E.m.f.	Actual E.m.f.	Difference between Calculated and Actual
133	Cu	51.34	52.20	+52.40				
	Ni	46.97						
		98.31						
	Mn	1.09	1.11	−4.00				
	Fe	0.43	0.44	−3.55	−8.55	44.05	43.88	+0.17
	Si	0.09	0.09	−0.75				
	C	0.04	0.04	−0.25				
134	Cu	51.68	52.60	+52.50				
	Ni	46.66						
		98.34						
	Mn	1.09	1.11	−4.00				
	Fe	0.38	0.39	−3.12	−8.30	44.20	44.26	−0.06
	Si	0.07	0.07	−0.58				
	C	0.09	0.09	−0.60				
135	Cu	51.77	52.70	+52.50				
	Ni	46.52						
		98.29						
	Mn	1.09	1.11	−4.00				
	Fe	0.40	0.41	−3.23	−8.59	43.91	44.69	−0.78
	Si	0.11	0.11	−0.90				
	C	0.07	0.07	−0.46				
136	Cu	51.57	52.50	+52.50				
	Ni	46.65						
		98.22						
	Mn	1.13	1.15	−4.15				
	Fe	0.45	0.46	−3.70	−9.00	43.50	44.03	−0.53
	Si	0.10	0.10	−0.82				
	C	0.05	0.05	−0.33				



No. 232. × 66. No. 236 × 66.



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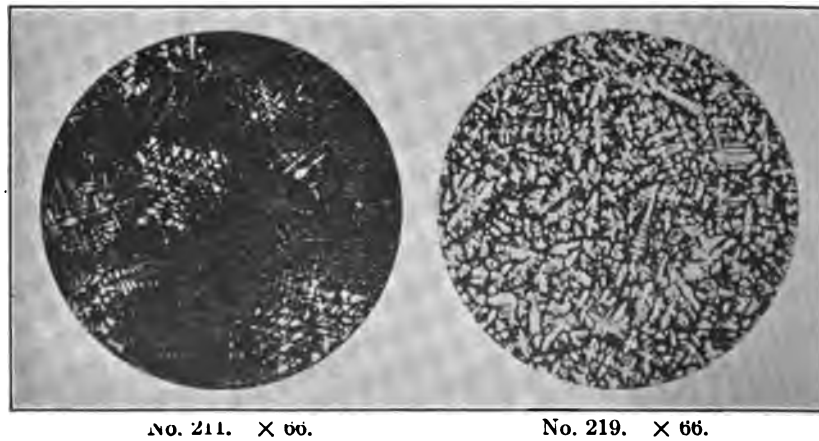
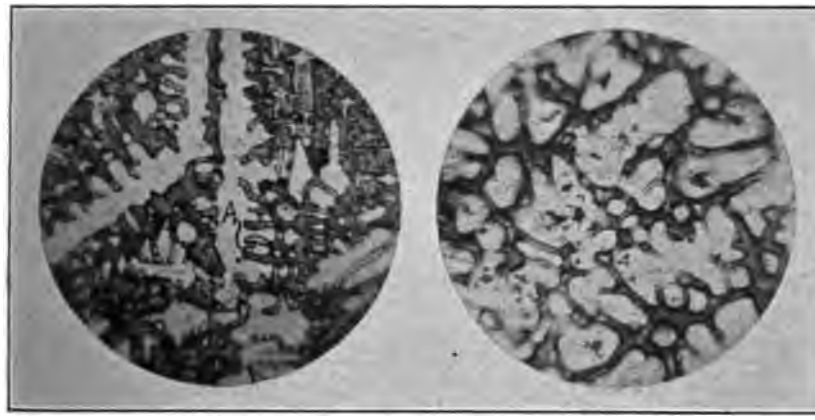


No. 211. × 66. No. 219. × 66.

FIG. 4.—CONSTANTAN MADE IN ELECTRIC FURNACE AND CAST IN IRON MOLDS.

ing this calculation is first to recalculate the analysis on the basis of the copper plus the nickel being equal to 100 per cent. The value of the e.m.f. given for that percentage of copper in Fig. 1 is set down in the partial e.m.f. column and under it the negative values caused by the presence of the impurities found in Figs. 2 and 3. The partial e.m.f's. are added algebraically and set down as the calculated e.m.f.

Through the courtesy of Mr. F. G. Weiss, vice-president and general manager of Hyatt Roller Bearing Division of General Motors Corpn. and Mr. J. G. Ayres, Jr., metallurgist, a number of photomicrographs were obtained of samples made in the electric furnace and cast in the iron mold as ¼ in. sq. bars. In Fig. 4 are shown photomicrographs Nos. 212, 226, 211, 232, 219, 236 which are of samples as cast, polished, and etched with hydrochloric acid and ferric chloride, as described.



No. 223. × 266. No. 225. × 266.

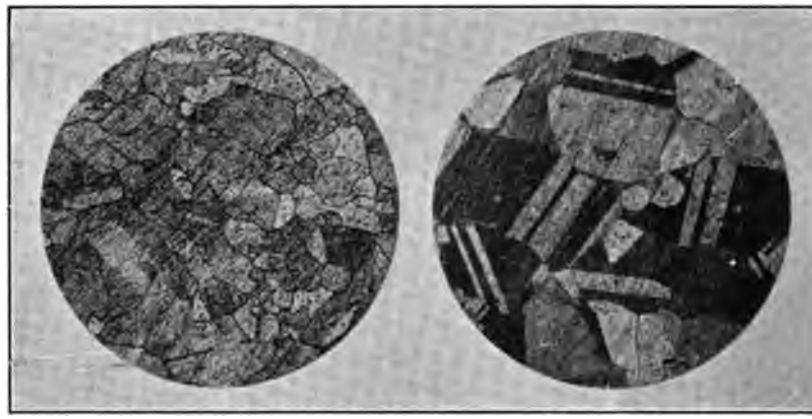
FIG. 5.—HIGH MAGNIFICATION OF CONSTANTAN SAMPLES.

The samples varied from a fine almost granular appearance (Nos. 212 and 226) to a pronounced dendritic structure (Nos. 211 and 219), and sometimes possessed a combination of these two extremes together with their intermediate structures. From the photomicrographs, it is apparent that as the constantan cools from the liquid state that the first crystals formed are relatively richer in nickel than in copper as the nickel has the higher melting point and that on further cooling, each subsequent set of solid solution crystals are richer in copper.

In Fig. 5, higher magnification (Nos. 223 and 225) shows that not only do the copper-nickel solid solution crystals vary in the relative amount of the two components, but that this variation, even within a given crystal, as shown at *A* of No. 223, is evidenced by the fact that the center of the crystal is light or contains higher nickel than the surrounding portions of the crystal.

Upon annealing two of the specimens (Nos. 227, 228) at 1750° F. (954° C.), for 1 hr. and allowing to cool in the furnace, very marked changes of structure occurred, as shown in Fig. 6. The primary structure has been almost entirely eliminated and is replaced by polyhedral grains. One interesting fact brought out is that the constantan alloy forms twinned crystals without being previously strained, as is generally the case with metals that show this structure.

The effect of impurities in the constantan is not apparent from the microstructure, although a more extended experimentation might show some results. Impurities could be seen in all samples, but they did not seem to affect the grain structure.



No. 227. × 66. No. 228. × 66.

FIG. 6.—SAMPLES AFTER ANNEALING AT 1750° F. FOR 1 HR. AND COOLING IN FURNACE

After all the experimentation with samples made in the small electric furnace, it was deemed advisable to take the problem to the mill and to run an experiment under the same conditions as those prevailing in the routine manufacture of constantan. The International Nickel Co. very kindly offered to run such an experiment at its plant at Bayonne, N. J., under the regular conditions. The test was planned as follows:

The melt was to be a regular 8000-lb. (3624 kg.) heat made under the same conditions as an ordinary production melt, with the exception that electrolytic nickel was to be used in place of shot nickel and thirteen small ladles of approximately 275 lb. each were to be tapped out to which different additions were to be made. From each of these small ladles, one test bar and one 4 by 4 by 40 in. (10.1 by 10.1 by 101.6 cm.) ingot were to be cast, the remainder of the metal was to be cast up as in a regular production melt. The additions to be made were as follows:

ADDITIONS FOR EXPERIMENTAL MELT

1½ oz. of magnesium for every 100 lb. of metal; 275 lb. ladles.
No. 1, No manganese, no iron.
No. 2, 0.25 per cent. manganese, no iron.
No. 3, 0.50 per cent. manganese, no iron.
No. 4, 0.75 per cent. manganese, no iron.
No. 5, 1.50 per cent. manganese, no iron.
No. 6, No manganese, 0.25 per cent. iron.
No. 7, 0.25 per cent. manganese, 0.25 per cent. iron.
No. 8, 0.50 per cent. manganese, 0.25 per cent. iron.
No. 9, 0.75 per cent. manganese, 0.25 per cent. iron.
No. 10, 0.50 per cent. manganese, 0.35 per cent. iron.
No. 11, 0.50 per cent. manganese, 0.45 per cent. iron.
No. 12, 0.50 per cent. manganese, 0.55 per cent. iron.
No. 13, 0.50 per cent. manganese, 0.50 per cent. silicon.
Remainder of melt, 0.50 per cent. manganese, no iron.

TEST AT BAYONNE, N. J.

The melt was made, as planned, in an oil-fired open-hearth furnace. The metals charged were electrolytic copper and electrolytic nickel, the proportion being approximately 46 per cent. nickel and 54 per cent. copper. When the metal was considered in a proper condition to pour, a small preheated ladle was set on a platform scales under the spout and the metal tapped into it. While pouring, the temperature of the stream was taken with a Leeds & Northrup optical pyrometer, the reading being made after the smoke and flame had cleared away and a clear sight of the stream could be had. The emissivity value of the constantan was estimated from temperatures taken in the furnace and readings on the stream and correction made to the apparent temperature to give the approximate true pouring temperatures. While tapping, the metal was poled and the additions were made; great precautions were taken to keep the metal from oxidizing while running down the spout, by covering with boards.

From each ladle was poured a test bar of 57 lb. (25 kg.) and a 200-lb. (90 kg.) ingot. The test bar was bottom-poured in a sand mold and had two fins cast on the side approximately 1 by 1 by 6 in. (2.5 by 2.5 by 15 cm.). One of these fins was cut off, machined smooth, and after sawing off a sample for photomicrographs, rolled to a strip ⅛ in. (3.1 mm.) thick from which a strip ¼ in. wide was sheared for electromotive force measurements. The test bar was also bored and the borings used for chemical analyses. While the ingot was poured, another temperature reading was made on the metal stream.

When the thirteen experimental ladles had been tapped, the scales were removed, a larger ladle was put under the spout, and the remainder of the metal tapped out and cast into nineteen ingots, nine ingots and a test bar being cast from the first ladleful.

Temperatures.—Temperature readings were made in the furnace by sighting at the wall above the tap hole through an observation hole in the wall on the opposite side. One reading was made through the flame, which probably gave the approximate flame temperature and the other on the brickwork just above the slag.

To calculate the emissivity, a number of assumptions had to be made as to the relation between the temperature of the walls and the temperature of the metal, as we had no closed-end tube to determine the true temperature of the metal in the ladle. However, even though the calculated true temperature is probably somewhat in error, all the values are comparative.

No readings could be made on the slag, as the flame interfered.

TABLE 1

Ladle No.	Tapping		Pouring		Remarks
	Apparent Temperature, Degrees F.	True Temperature, Degrees F.	Apparent Temperature, Degrees F.	True Temperature, Degrees F.	
		2892			Back wall
		3050			Flame
1	2300	2560	2223	2472	
2	2300	2560	2233	2483	
3	2345	2620	2281	2540	
4	2348	2620	2348	2618	
5	2367	2640	2338	2608	
6	2367	2640	2328	2595	
7	2376	2650	2348	2618	
8	2411	2695	2395	2675	
9	2411	2695	2376	2650	
10	2420	2704	2403	2683	
11	2420	2704	2395	2675	
12	2436	2724	2420	2704	
13	2445	2735	2462	2763	
14	2503	2803	2486	2783	First ingot
14			2470	2767	Fifth ingot
14			2445	2735	Eighth ingot

NOTE.—The true temperature was calculated for an emissivity of 0.28, using Wien's law $\log E = \frac{c_2}{\lambda} \log e \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ where E = emissivity; $c_2 = 14{,}500$; e = base of Napierian logarithms; λ = wave-length of light used, 0.65μ; T_1 = apparent temperature absolute; T_2 = true temperature absolute. The curve of apparent temperatures plotted against true temperature is given in Fig. 7.

In Fig. 8 are plotted tapping and pouring temperatures for each ladle.

E.m.f. Measurements.—The samples prepared from the test bar of each ladle were annealed and tested against the standard iron-constantan couple for electromotive force. These results, together with the analyses,

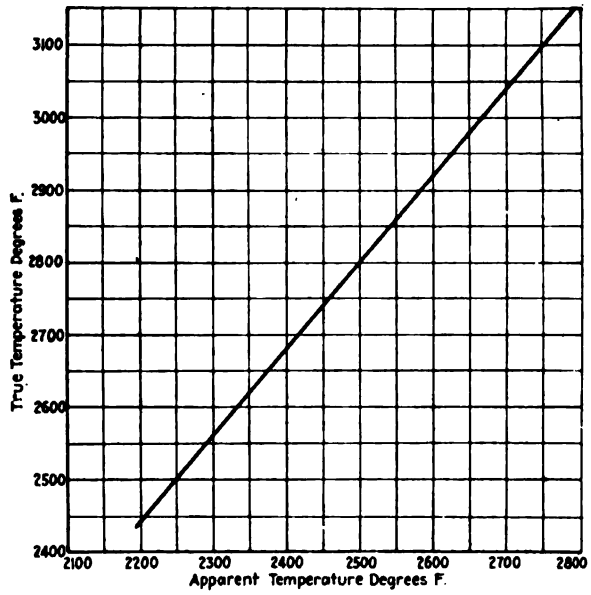


FIG. 7.—APPARENT VS. TRUE TEMPERATURES FOR CONSTANTAN FOR $\lambda = 0.65\mu$.

are given in Table 2. The Leeds & Northrup Co. specifications require that constantan, to be acceptable, must give an e.m.f. with pure iron of 47.40 $\pm$ 0.50 millivolts of 1500° F., or come within 15° F. of the true

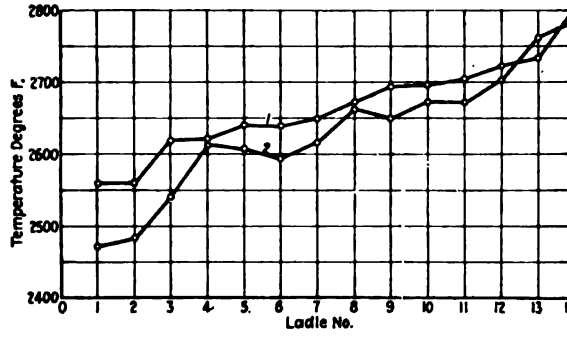


FIG. 8.—TAPPING AND POURING TEMPERATURES OF CONSTANTAN MELT C-141. 1. TAPPING TEMPERATURES. 2. POURING TEMPERATURES.

temperature when the standard millivolt temperature curve is used. The e.m.f. of pure 55–45 copper nickel against iron at 1500° F. is 53.25 millivolts.

TABLE 2.—*Results of E.m.f. Measurements*

Ladle No.	Total Wt., Pounds.	Copper, Per. Cent.	Nickel, Per Cent.	Iron, Per Cent.	Carbon, Per Cent.	Sulfur, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Divergence from Standard, Degrees F.	Millivolts Below 55-45 Copper-nickel.
					Melt C141					
1	307.5	54.86	44.76	0.11	0.24	0.004	....	0.02	+89	3.08
2	291.0	53.86	45.42	0.14	0.28	0.004	0.25	0.03	+63	3.65
3	264.75	53.61	45.40	0.15	0.24	0.009	0.55	0.03	+5	5.69
4	265.0	52.45	46.34	0.15	0.24	0.005	0.78	0.02	−24	6.69
5	278.0	51.67	46.35	0.17	0.27	0.005	1.50	0.03	−88	8.93
6	273.0	52.57	46.84	0.23	0.29	0.005	0.03	0.02	−33	7.60
7	289.5	52.22	46.73	0.25	0.23	0.008	0.26	0.02	−7	6.10
8	276.0	51.88	47.34	0.22	0.28	0.005	0.53	0.02	+1	5.80
9	283.0	51.74	46.97	0.23	0.25	0.004	0.77	0.03	−42	7.32
10	284.0	52.55	46.35	0.28	0.23	0.006	0.52	0.04	−29	6.87
11	285.0	53.02	45.78	0.40	0.23	0.006	0.52	0.03	−60	7.95
12	280.0	53.22	45.46	0.49	0.21	0.005	0.54	0.05	−72	8.37
13	275.0	52.87	45.44	0.18	0.22	0.012	0.54	0.72	−135	10.58
14	3828.0	53.21	45.84	0.17	0.22	0.008	0.47	0.07	+3	5.74
15	.....	58.46	41.17	0.10	0.24	0.005	?	0.01		
					Melt Analyses					
Melt 111		53.14	45.37	0.31	0.08	0.019	0.95	0.11	−16	−6.35
Melt 119		53.22	44.98	0.38	0.08	0.015	1.19	0.12	.....	..... Average of
Melt 120		53.17	45.17	0.39	0.09	0.011	1.07	0.09	−35	−7.08 Wire
Melt 121		53.81	44.58	0.36	0.06	0.010	1.06	0.10		
Melt 133		51.34	46.97	0.43	0.04	0.020	1.09	0.09	−100	−9.35 Test Bar
Melt 134		51.68	46.66	0.38	0.08	0.026	1.09	0.07	−89	−8.47 Test Bar
Melt 135		51.77	46.52	0.40	0.07	0.019	1.09	0.11	−77	−8.84 Test Bar
Melt 136		51.57	46.65	0.45	0.05	0.020	1.13	0.10	−96	−9.21 Test Bar
Melt 137		52.10	46.20	0.46	0.11	0.17	0.62	0.13	−93	−9.10 Test Bar
Melt 141		53.21	45.84	0.17	0.22	0.008	0.47	0.07	+3	5.76 Test Bar
Melt 142		52.85	45.74	0.35	0.06	0.019	0.85	0.12	−69	−8.26 Test Bar
Melt 143		52.34	46.46	0.35	0.07	0.018	0.68	0.07	−20	−6.55 Test Bar
Melt 144		53.12	45.93	0.29	0.07	0.016	0.50	0.07	+12	..... Test Bar
Melt 145		53.52	45.37	0.34	0.12	0.012	0.53	0.10	−40	..... Test Bar
Melt 146		53.55	45.42	0.32	0.06	0.014	0.54	0.08	0	..... Test Bar
Melt 147		53.66	45.40	0.30	0.07	0.015	0.47	0.07	−21	..... Test Bar
Melt 148		53.24	45.78	0.32	0.07	0.017	0.50	0.06	+22	..... Test Bar
Melt 149		53.43	45.54	0.32	0.08	0.016	0.52	0.06	+33	..... Test Bar
Melt 150		53.48	45.48	0.32	0.06	0.017	0.57	0.06	+27	..... Test Bar

All the e.m.f. measurements that were made on the thirteen experimental ladles of melt C141 were made on the fin cut from the test bar, which was bored for chemical analysis, so that we can say the analysis given is that of the piece tested. In the case of regular production melts, however, the analysis is the mean of all the ladles for that melt and the e.m.f check was made on a sample cut from one test bar only, so that the analysis for the melt probably is somewhat different from that of the piece on which the e.m.f. measurements were made.

In Table 2, the different ladles that are grouped together are the ones wherein different elements were varied. For instance, in ladles 2, 3, 4, and 5 only the manganese was varied, the iron being held as low as possible. In ladles 6, 7, 8, and 9, it was attempted to hold the iron to 0.25 per cent. while the manganese was varied. It should be noted how

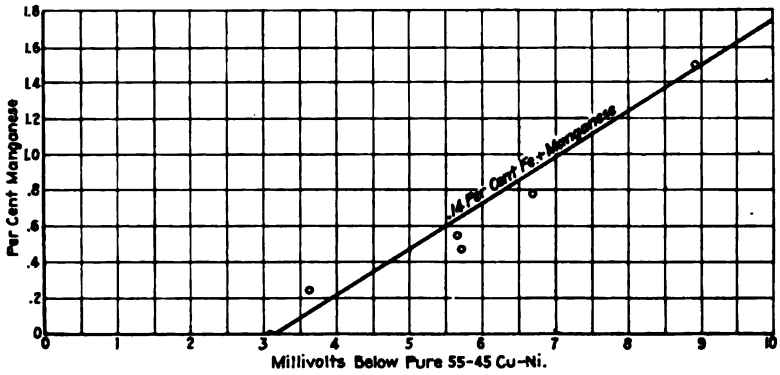


FIG. 9.—MILLIVOLT DROP CAUSED BY ADDITION OF MANGANESE TO MELT C-141. IRON HELD CONSTANT AT 0.14 PER CENT.

closely the operators were able to control the manganese, a surprising accuracy being obtained. In the case of iron, however, in ladles 10, 11, and 12 such accuracy was not attainable.

Table 2 also gives a number of melt analyses with e.m.f. tests. On examining the analyses from C144 on, it will be noted how closely the melter was able to control his iron and manganese content; the iron only varied 0.05 per cent. throughout and the manganese 0.10 per cent. The iron is the most important element to control as 0.1 per cent. of iron roughly equals 0.2 per cent. of manganese in its effect on the thermoelectric properties of constantan. It will also be noted that for melt C141, the low figure of 0.17 per cent. was reported for iron. This was due to the fact that the melt was made from electrolytic nickel.

In Figs. 9, 10, and 11 are plotted the results of the e.m.f. measurements. Fig. 9 shows the e.m.f. variations for variation of manganese, the iron composition being held at 0.14 per cent. The points fall fairly close to a straight line, which is the shape of curve we would expect from

experimental melts made previously. The standard e.m.f. is 5.85 millivolts below pure 55-45 copper-nickel and the allowable variation is 0.5 millivolts below and above that. Fig. 10 shows the curve for 0.23 per cent. iron with variation of manganese. This curve is drawn parallel to the 0.14 per cent. iron but is very poorly defined. Fig. 11 shows the

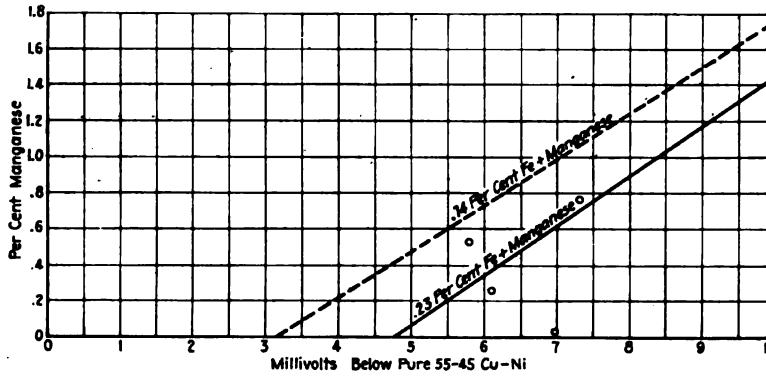


FIG. 10.—MILLIVOLT DROP CAUSED BY ADDITION OF MANGANESE TO MELT C-141. IRON HELD CONSTANT AT 0.23 PER CENT.

curve for variation of iron, holding manganese constant at 0.50 per cent. This curve is very well defined. It is probable that the reason that the curves showing variation of e.m.f. with variation of manganese are not well defined by the points is because manganese acts as a scavenger and for that reason all does not take effect.

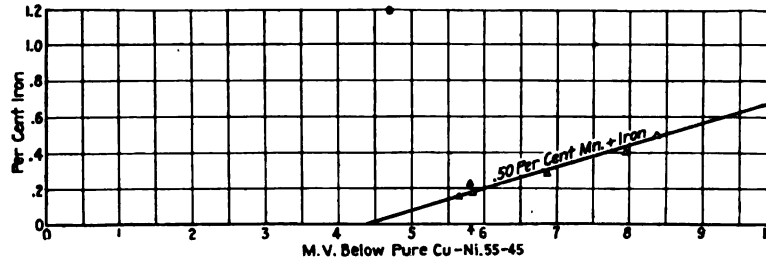


FIG. 11.—MILLIVOLT DROP CAUSED BY ADDITION OF IRON TO MELT C-141. MANGANESE HELD CONSTANT AT 0.50 PER CENT.

Photomicrographs of samples from the thirteen experimental ladles of which the two (Nos. 233 and 235) in Fig. 12 are representative were taken and a number also made of annealed samples. It was very surprising to note that in the annealed specimens there was no change in grain structure. The annealing was repeated two and three times with the same results. As will be remembered these samples were cut from the test pieces which were sand cast and cooled much more slowly than the chill-cast specimens made in the small furnace. The sand-cast con-

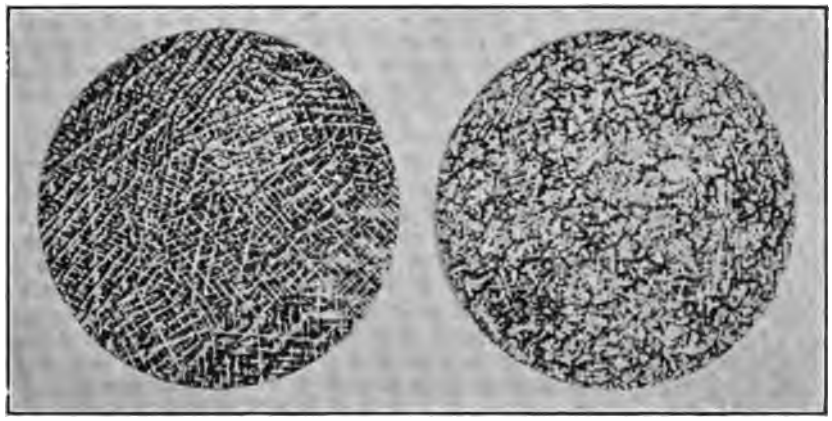
stantan had a much larger grain size, as will be seen by the magnification. No attempt is made to explain this as a much more exhaustive test would have to be made to draw any satisfactory conclusions.

TABLE 3.—*Checks on No. 8 Wire from Melts* C141 *and* C143

Coil No.	Divergence from Standard, Degrees F.	Coil No.	Divergence from Standard, Degrees F.	Coil No.	Divergence from Standard, Degrees F.	Coil No.	Divergence from Standard, Degrees F.
1	− 8	39	+18	76	− 4	113	+36
2	− 2	40	−10	77	− 2	114	+41
3	−12	41*	−10	78	+30	115	− 7
4	−13	42	− 4	79	+26	116	− 3
5	−14	43	+ 1	80	+42	117	−12
6	− 4	44	+ 1	81	+31	118	− 3
7	−12	45*	−20	82	− 5	119	+34
8	− 2	46	− 3	83*	+45	120	+ 2
9	+42	47*	− 6	84*	0	121	− 4
10	−40	48	+23	85	− 5	122	− 9
11	−10	49*	− 5	86*	0	123	+ 4
12	+35	50*	0	87*	+37	124	− 1
13	+35	51*	+38	88	+36	125	− 3
14	− 8	52	− 3	89	− 1	126	+40
15	−10	53*	+38	90	− 3	127*	+24
16	− 1	54	− 4	91	− 6	128	+ 4
17	− 4	55	+30	92	− 5	129	− 2
18	− 8	56	− 3	93	− 3	130	+40
19*	−10	57	+22	94	− 3	131*	+25
20	+35	58	− 9	95	− 5	132	+ 3
21	−14	59*	−20	96	− 4	133	− 2
22	− 1	60	+22	97	− 5	134	− 7
23	+30	61	+ 2	98*	−20	135	+ 2
24	−10	62*	+40	99	+25	136	+36
25	−10	63*	+ 3	100	− 6	137	− 8
26	0	64	+23	101	+ 1	138*	+50
27	0	65	− 7	102*	−33	139	− 4
28	−10	66*	+ 2	103	− 2	140	− 6
29	− 5	67*	+ 3	104	−17	141	0
30	− 7	68	− 4	105	−13	142	+26
31	+14	69	− 3	106*	− 5	143	+36
32	+21	70*	+44	107*	− 5	144	− 1
33	+37	71	+29	108	− 2	145	+43
34	−11	72	− 9	109	− 2	146*	+ 7
35	− 1	73	+29	110	− 1	147	+38
36	− 4	74	− 1	111	+ 4	148*	+ 4
37	0	75	+45	112	0	149	−20
38	− 1						

Average value = +5.3° F. * Sample taken for analysis.

Wire Tests.—The production ingots from melts C141 and C143 were rolled and drawn down to No. 8 B. & S. gage wire, of which there were 149 coils averaging about 62 lb. (28 kg.) to the coil. These were all tested at 1500° F. (816° C.) against iron-constantan couples, with results given in Table 3. Ten samples of wire were selected, carefully checked, and then cut up for analyses. The numbers and checks on the samples are given in Table 4.



No. 233. × 16. No. 235. × 16.

FIG. 12.

TABLE 4.—*Analyses of Constantan Sample Wire*

Sample No.	Temperature Error, Degrees F.	Copper, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Manganese, Per Cent.	Carbon, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.
75	+46 above standard.	53.08	46.01	0.16	0.45	.....	0.06	0.03
87	+39 above standard.	53.21	45.89	0.15	0.44	0.22	0.11	
51	+32 above standard.	53.29	45.83	0.16	0.43	....	0.08	
48	+16 above standard.	52.74	46.28	0.16	0.51	....	0.11	
146	+7 above standard.	53.01	45.76	0.44	0.63	0.08	0.053	0.023
63	+3 above standard.	52.95	45.91	0.36	0.62			
106	−4 below standard.	52.75	46.00	0.38	0.70	0.07	0.08	
127	−8 below standard.	52.91	45.89	0.36	0.69	....	0.14	
5	−17 below standard.	52.85	45.90	0.36	0.73	....	0.13	
59	−24 below standard.	51.98	47.03	0.23	0.62	....	0.22	
Mean...	+9 above standard.	52.88	46.05	0.276	0.582	0.130	0.109	

A composite sample was made from Nos. 75, 87, 51, and 48 and the carbon determined was 0.22 per cent. In a composite sample made from Nos. 146, 63, 106, 127, 5, and 59 the carbon was 0.07 per cent.

In Table 5 are tabulated the mean of the analyses and checks given in Table 4, the weighted average of the analyses of melts C141-14, C141-15 and C143, with the average of all wire checks on those two melts

and the average analyses of ladles Nos. 1 to 13 of melt C141 with the average of the checks made on test pieces from those ladles.

TABLE 5.—*Mean of Analyses and Checks*

Mean from	Copper, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Manganese, Per Cent.	Carbon, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Mean Temperature Error, Degrees F
Table 4.....	52.88	46.05	0.276	0.582	0.130	0.109	0.026	+ 9
C141 and C143.....	53.85	44.99	0.276	0.717	0.119	0.092	0.014	+ 5.3
C141, 1 to 13.....	52.82	46.09	0.231	0.522	0.25	0.08	0.006	−26
Mean.....	53.18	45.71	0.261	0.607	0.166	0.093	0.015	− 4

These averages represent 15,000 lb. of constantan, 26 analyses, and 172 e.m.f. measurements and for that reason should show as closely as possible the relation between composition and electromotive force.

Two-thirds of the wire resulting from melts C141 and C143, on which the average temperature error is +5.3° F., was acceptable and of 40,000 lb. tested later, which was made to specifications estimated from the data taken, 25 per cent. was acceptable; that is, checked within + or ±0.5 millivolts of standard. From this it will be seen that it is possible to obtain satisfactory thermocouple wire by selection if specifications are calculated from the experimental data. The reason it is not possible to get a larger per cent. is due to small unavoidable variations in impurities, such as iron from tools, or perhaps all the manganese does not go into solution or the silicon runs a little high, etc.

From the tests on samples from melts C141 and C143 as cast and the finished wire it is shown conclusively that the mechanical working and annealing have no effect whatever on the thermal e.m.f. or chemical composition. To show the differences that may occur in e.m.f. calculated from the chemical analysis, a piece of No. 8 B. & S. gage wire 30 in. (76 cm.) long was carefully checked for thermal e.m.f. It was then flattened into strips, cut into small pieces, carefully sampled, and two of the samples sent to two good chemists. Their analyses and e.m.f. calculated from the data in each case are given in Table 6.

TABLE 6

	Copper, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Manganese, Per Cent.	Carbon, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Calculated E.m.f.	Actual E.m.f.
A	53.01	45.76	0.44	0.63	0.08	0.053	0.023	45.25	47.64
B	52.75	46.30	0.25	0.45	0.08	0.08	0.04	47.63	47.64

The difference of iron and manganese reported in the two cases make a large difference in the e.m.f. so that the best that can be expected on a heat is to strike an average and be able to select from it material that will meet specifications. The calculated e.m.f. of the average of a number of heat analyses will come fairly close to the average of thermal e.m.f. checks, as can be seen by referring to Table 5. In general, it can usually be prophesied which of two melts will run lowest in e.m.f. and differences can be accounted for roughly but not exactly for the reasons stated above.

Throughout the above investigation, The International Nickel Co. and the Electrical Alloys Co. showed the heartiest coöperation and interest in the development of satisfactory thermocouple wire and expressed a desire to assist in furnishing, wherever possible, an American product for American consumers. The writer wishes particularly to thank Dr. John F. Thompson of the International Nickel Co., Mr. F. V. Lindsley of the Electrical Alloys Co., and Prof. M. A. Hunter for their suggestions and assistance, which helped materially in concluding this investigation successfully.

Manufacture and Electrical Properties of Manganin

BY F. E. BASH,* CH. E., PHILADELPHIA, PA.

(Philadelphia Meeting, September, 1919)

PREVIOUS to the war, this country depended on Europe for its supply of a number of alloys of great importance in the manufacture of electrical apparatus and equipment. When this source was cut off shortly after the beginning of hostilities and the small stocks in the United States were exhausted, either inferior substitutes had to be used or the manufacture of the apparatus suspended. Since electrical equipment was of primary importance in the prosecution of the war, the substitutes had to be used until the composition and processes of manufacture of the alloys could be determined. Included among these alloys was one generally known as manganin, which is composed chiefly of copper and manganese and which, beside having a low-temperature coefficient of resistance, has a low thermal electromotive force against copper. These qualities make it valuable for the manufacture of electrical instruments and machines in which it is used in the shape of wire, rod, and strip.

As a result of these circumstances, an investigation was started to determine how manganin could be made on a commercial basis so that a product of uniform quality and the necessary electrical characteristics could be produced. The object was to procure an alloy with temperature coefficient of resistance not greater than $\mp 1 \times 10^{-5}$ per ° C. and a thermal e.m.f. against copper no greater than that of the imported material.

It is characteristic of manganin that the temperature-resistance curve is not a straight line but has a peak, which varies in position with different samples; it is most desirable, however, to have it at a temperature of 25° C. if possible. The coefficients of manganin from all records available ranged from a large negative to a large positive value. The composition as reported by different authorities is given in Table 1. Prof. Matthew A. Hunter, of Rensselaer Polytechnic Institute, made up a number of small melts of manganin in a graphite crucible and the one that he reported as having the best coefficient gave the following analysis: Copper, 83.6 per cent.; nickel 2.5 per cent.; manganese, 13.6 per cent.; iron, 0.3 per cent. An analysis of a sample of German manganin gave the following: Copper, 82.6 per cent.; nickel, 3.8 per cent.; manganese, 12.8 per cent.; iron 0.7 per cent.

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* Research Engineer, Leeds & Northrup Co.

TABLE 1.—*Composition of Manganin*

Authority	Copper, Per Cent.	Nickel, Per Cent.	Manganese, Per Cent.
Kaye & Laby	84	4	12
Standard handbook	65	5	30
Foster	85	3	12
Liddell	84	4	12
Nichols	78.3	7.6	14.1
Nichols	51.5	16.2	31.3
Perrine	70.0	5	25
Perrine	65	5	30
Feussner-Lindeck	73	3	24
Lindeck	84	4	12
Dewar & Fleming	84	4	12
Feussner-Lindeck	86	2	12

Since it had been found from previous experience on other electrical alloys that small impurities often had a large effect on electrical properties, it was decided to first make up a number of melts in the reducing atmosphere of the granulated-carbon resistor-type electric furnace and to use alundum crucibles in which to make the melts. Bars $\frac{3}{8}$ in. (9.5 mm.) square by 6 in. (15 cm.) long were cast in an iron mold and a pair of hand-operated rolls served to reduce them to a wire 0.1 in. square, in which form the alloys could very easily be tested for temperature coefficient by the use of a Kelvin bridge. An electric wire resistor furnace was used for annealing work. The materials used were all as pure as could be obtained, electrolytic nickel and copper, Goldschmidt manganese, and iron 99.7 per cent. pure in the shape of fine wire.

On carrying out preliminary experiments to determine the best method of annealing, it was found that prolonged heating at high temperatures materially affected the coefficient. Illuminating gas, carbon dioxide, vacuum, open air, and the quiet slightly oxidizing atmosphere of an electric wire resistor furnace were tried. The latter treatment was finally adopted as being simple and giving good results when temperatures of approximately 1500° F. were used.

The first melt showed a peak, or point of maximum resistance, at 15° C., which was too low although the coefficient was good. It was then decided to change the amount of iron and keep all the other elements constant, to determine if it would not be possible to shift the peak by varying the iron. A number of melts were made and the iron content varied from 0.2 to 2.0 per cent. Coefficient curves on each of the samples prepared showed that increasing iron content increased the temperature at which the peak occurred, but that more than 1.5 per cent. iron caused that temperature to decrease. Since 1.5 per cent. iron gave a peak at 25° C. where it was most desirable, that value was decided on and the for-

mula below adopted, since it gave the following coefficients; 15–30° C. + 0.0000030 per 1° C.; 15–45° C. − 0.0000038 per 1° C. This alloy consisted of electrolytic copper 83.0 parts, nickel 2.5 parts, Goldschmidt manganese 14.0 parts, pure iron 1.5 parts; total, 101.00 parts.

Melts of this composition were made up in a small graphite crucible to determine its effect but they were so brittle from the silicon picked up that it was impossible to roll them. The silicon also affects the electrical properties of the manganin even when present in as small quantities as 0.1 per cent.

After sufficient data had been obtained in the electric furnace with the small crucibles, which only held 100 gm., a number of 25-lb. (11-kg.) melts were made in a gas-fired furnace in different kinds of crucibles in an effort to reproduce the results of the small melts on a larger scale. Clay, sand, and graphite crucibles were tried, but they distorted the temperature-resistance curve by adding silicon, and, with the exception of the graphite, were all badly cut at the metal line by the charcoal used to keep the metal reduced. Alundum crucibles could not be obtained and would have been too expensive anyway, so a graphite crucible was lined with magnesia and a melt made. This proved to be practically an exact reproduction in electrical properties of the 100-gm. melt made in alundum and four successive heats gave the same results. It was concluded that it would be practical to repeat results if the proper precautions were taken and no injurious impurities such as silicon introduced into the metal. The only objection to melting in magnesia-lined crucibles is that the lining does not adhere readily to the graphite and shrinks away to such an extent that it has to be repaired after each melt, although that is not a particularly difficult or lengthy process.

Later, a graphite crucible was tried which was lined with alumina mixed with kaolin but very poor results were obtained.

The melting practice followed in these tests was as follows: The copper and nickel were charged at the same time and, after melting, the metal was covered with charcoal. The manganese was divided into two portions which were carefully stirred in with an iron rod, enough time being allowed for the first portion to melt before the second portion was added. Care was also taken not to let the iron rod get so hot that it would dissolve. The metal was then allowed to heat up, after which the iron was added as fine wire or very thin sheet cut into small pieces and thoroughly stirred in. After time was allowed for the iron to dissolve, the metal was deoxidized with magnesium by tying pieces of it to an iron rod with copper wire and plunging it to the bottom of the crucible containing the manganin. The amount of magnesium used was 0.1 per cent. by weight of the charge. After deoxidizing, the metal was immediately poured into iron molds. Careful deoxidation is very essential as a small amount of oxygen has a great effect on its electrical proper-

ties. This may possibly be due to the fact that 0.4 per cent. of oxygen forms an eutectic with copper.

To further determine if manganin with the above-specified electrical properties could be duplicated, instructions for making it were given to a metal manufacturer; which resulted in his making some excellent material with the proper coefficient in both wire and rod form.

It is thought by some users of manganin that it can be made in almost any manner with a large variation in composition but that the mechanical working will have a great effect on its temperature coefficient. This is not true in regard to the composition and melting or in regard to the working if the proper precautions are taken. When manganin is annealed in an oxidizing atmosphere, the manganese on its surface selectively oxidizes and leaves a highly conducting film or sheath of copper. If the material is in the form of wire, the copper on its surface, which is a very much better conductor than manganin, carries an appreciable percentage of the electrical current. Copper having a high positive temperature coefficient makes the coefficient of the wire positive. If now that wire is dipped into acid for a few seconds, the copper sheath dissolves and the wire has the same coefficient as before. If instead of pickling, the wire is drawn through a die, some of the outside coating is scraped off and tends to make the coefficient less positive so that different results will be obtained when the wire is not pickled.

To determine the effect of working, the coefficient of a bar was taken as it was cast. The bar was then drawn down to 0.002 in. (0.05 mm.) diameter and retested; the coefficient of the wire was found to be the same as that of the bar.

A wire made from one of the experimental melts and a German made wire tested for thermal e.m.f. against copper gave the following results:

AVERAGE THERMAL E.M.F. FROM 0 TO 100° C.

	VOLTS PER DEGREE C.
Imported wire	13×10^{-6}
American wire	5.6×10^{-6}

It is very desirable that a resistance material used for shunts and coils have a low thermal e.m.f. against copper; from the above it can be seen that the American wire has less than one-half the e.m.f. of the imported wire.

SUMMARY OF RESULTS

In the following when "coefficient" is spoken of, the temperature coefficient of resistance between 15° and 30° C. is meant. As before stated, it is a characteristic of manganin that the temperature resistance curve has a point of maximum resistance. For good material, the slope of the curve on both sides of the maximum is small and for poor material the slope is steep.

1. Effect of constituents on temperature coefficient of resistance. Small variations in manganese content do not materially affect the coefficient. It causes a change in resistivity and tends to make the coefficient more negative.

No experiments were made with varying nickel content although the writer has taken the coefficient of one sample, which had the following analysis: Copper, 84.06 per cent.; iron, 0.71 per cent.; manganese, 14.76 per cent.; silicon, 0.47 per cent. This material had a good coefficient but would probably be hard to reproduce due to variation in silicon.

The effect of iron is very marked. It will shift the point of maximum resistance and will make the coefficient more negative if added in too large quantities.

Silicon is such a varying factor that it cannot be controlled and allowed for. If uniform results are desired, it is better to keep it out altogether. Its effect is to make the slope of the temperature resistance curve greater and, in general, to make the coefficient more negative.

Oxygen has a very marked effect on the coefficient and tends to make it strongly positive.

Carbon appears to have no effect on the coefficient and tends to reduce oxides.

2. Clay-graphite crucibles add silicon and for that reason are undesirable. Clay crucibles are undesirable for the same reason. Alundum crucibles are satisfactory but expensive. Magnesia or magnesia-lined graphite crucibles are entirely satisfactory.

3. Annealing in vacuum gives good results but is unnecessary. Annealing in CO_2 gives good results. Annealing in open air causes oxidation of manganese and increases the temperature coefficient. Annealing in an electric wire resistor furnace is simple and gives good results. Any annealing where oxygen is present necessitates pickling afterward to restore the temperature coefficient. It is only necessary to anneal a few minutes at 1500° F. to produce proper results.

4. Electrolytic copper is easily obtained and is most desirable to use. Electrolytic nickel is most desirable but if the iron content of shot nickel is allowed for it can be safely used. Goldschmidt manganese is most desirable as it has a low percentage of silicon and high manganese content.

5. Successive melts show that electrical properties can be reproduced if reasonable care is exercised. Silicon and oxygen must be kept as low as possible. A coefficient better than the best imported manganin may be obtained and can be reproduced in wire, bar, or sheet form. The thermal e.m.f. against copper of the manganin made is less than one-half that of the imported material. Hard drawing does not materially affect the coefficient but the manganin must be aged at a low temperature to take out strains before using or the resistance will not remain constant.

In Fig. 1 are shown the temperature-resistance curves of various samples of manganin. *F* is a sample of the best German manganin. *18* and *3* are curves showing samples strongly positive and negative in coefficient. *9* is a curve of a 50-gm. melt made in the electric furnace and *19* is a curve of a 25-lb. melt made in a gas furnace. It is possible to make man-

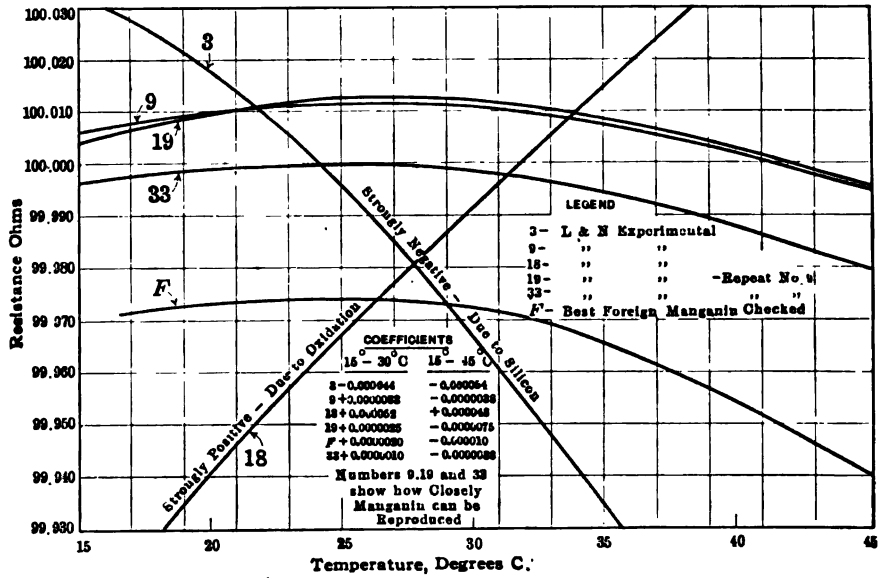

FIG. 1.—TEMPERATURE COEFFICIENTS OF MANGANIN.

ganin of varying compositions and still have a good coefficient but to make an alloy of which the electrical properties can be reproduced with assurance, the variable elements such as silicon must be eliminated.

In conclusion the writer wishes to thank Dr. Matthew A. Hunter and Dr. F. E. Carter for their coöperation and suggestions.

DISCUSSION

F. WENNER,* Washington, D. C. (written discussion).—For electrical measuring instruments, especially those types that involve the Wheatstone bridge or potentiometer principle and standards of electrical resistance, there has been, for a considerable time, a need for better resistance materials. For a satisfactory resistance material, much depends on the purposes for which it is to be used. For potentiometers and Wheatstone bridges, such as are in more or less general use, and the more common forms of resistance standards, a good quality of manganin answers fairly well. However, it should not be presumed that manganin is considered

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ideal for the purpose, for in measuring instruments and resistance standards, there is still much to be desired. An experience of more than 10 years in the study of the resistance standards and resistance apparatus shows that manganin resistances change with time in a way that is very annoying and the maintenance of the unit of resistance to the desired accuracy requires an excessive amount of work or may be said to be practically impossible. The changes in resistance are generally most rapid and erratic in resistances of very low and very high values. In resistances of low value, the resistance material is often in the form of thin sheets so that the surface is large and usually more or less unprotected from the atmosphere, or the oil in the case of oil-immersed standards. In resistances of high value, the resistance material is in the form of fine wire and, therefore, the surface is large compared with the cross-section. In resistances of medium value, the surface is less, compared with the cross-section, or better protected, usually by a silk wrapping impregnated with shellac. This suggests that one of the difficulties with manganin is slow surface action or oxidation, even when an effort has been made to protect the surface from such action However, the changes observed cannot all be accounted for on this basis. There are, presumably, also some internal changes in the resistance material even when it has been annealed. Further, the changes in manganin resistances seem to be more or less independent of its electrical properties. In other respects, too, manganin is not ideal.

What is desired is a material having an electrical resistance or resistivity that will remain constant with time to the highest possible degree; a high resistance to surface action or oxidation; high resistivity; a very small resistance-temperature coefficient; very small thermoelectromotive force against copper; good mechanical properties, so that it can be easily drawn or rolled, silver soldered or brazed, and wound in coils even when in the form of very fine wire; and cost of producing which is not excessive. Of course no one material can possess all of these properties to the extent desired; one or more of them must be sacrificed to get more nearly what is desired of another. A good quality of manganin possesses most of these properties to a remarkable degree. However, other alloys may be found that possess many of these properties to a greater degree.

In a number of resistance standards the resistance material has the following composition: Copper, 84.2 per cent.; aluminum, 4.2 per cent.; manganese, 11.5 per cent.; nickel, trace; iron, trace. This, it will be observed, is similar to manganin except that the nickel is replaced by aluminum. In so far as the resistivity and temperature-resistance coefficient are concerned, this material is practically the equivalent of manganin. The thermoelectromotive force against copper is less than that of manganin against copper. The value we have found using different lots of the material is about 0.3 microvolt per degree centigrade,

which is only about 0.1 as large as for the best of the manganin. This material is, therefore, considerably better than manganin in this respect. which is an important one where the resistance is of very low value. Mechanically, this material is considerably better than manganin. Our observations on the constancy of the resistance are not very conclusive, since during the past few years this work has not received the attention it would have received under normal conditions. However, the indications are that the standards in which this material was used are as reliable as those in which manganin was used. There is, therefore, every reason to think that this alloy constitutes a very promising field for investigation.

An alloy of gold and palladium (about 60 per cent. gold and 40 per cent. palladium) has fairly good electric properties and there is a possibility that for resistances made from extremely fine wire it may prove superior to any of the alloys that have been used for this purpose. At any rate, we would expect the surface action to be much less than for manganin or similar alloys.

For certain types of resistances, some consider an alloy of nickel and copper, which might be classed as constantan, better than manganin. An investigation of this alloy from the standpoint of its resistance properties might lead to the development of a better material for use in the construction of high resistances and resistances to be used with alternating current.

The work done by Mr. Bash is of very great importance to all concerned in the use of resistance material and is, no doubt, of equal importance to those concerned in making other alloys of a definite and uniform composition. However, we should not presume that all that is desired in the production of electrical resistance material has been done. There is need for similar work with other alloys and the development of new alloys which will possess some or all of the properties mentioned to a greater degree than does manganin. There is, therefore, plenty of room for more work along this line. Finally, the proof of the real quality of any of these alloys is the constancy of the resistances constructed from them; in the case of good alloys, this requires a series of measurements extending over several years.

F. G. SMITH, Waterbury, Conn.—I would like to ask whether small amounts of iron give the maximum resistance at a low temperature, and if the large amounts of iron raise the temperature at which the maximum resistance occurs? That is, with a small amount of iron, will a maximum be at, say, 10°?

F. E. BASH.—With the small amount of iron, the maximum is at a lower temperature, and with the increase of iron, the maximum increases; it seems to come to a maximum and then decrease; that is, increasing

the iron up to a certain value increases the temperature at which there is a maximum of resistance, and any increase of iron beyond that value will start decreasing this temperature. With 2 per cent. of iron, the maximum is lower than for 1.5 per cent. which was the value that we found to be satisfactory.

F. L. DRIVER,* Jr., Harrison, N. J.—I would like to ask what chance there is of the instrument companies getting together and deciding on standards for both manganin and constantan? We make both of these alloys in this country and we find that each one of the instrument companies who buy these materials require different standards of specific electrical resistance and thermal e.m.f. For instance, some of our customers require an electrical resistance in manganin or therlo of 240 ohms per circular mil foot and others require it with a specific electrical resistance of 270 ohms per circular mil foot. They buy these alloys in relatively small quantities so that it means much extra melting and supervision when making up small quantities for each consumer. If something could be done to eliminate this, it would be a benefit to the instrument companies, who could secure their material more cheaply, and to the manufacturers, who would not have to spend so much time and effort in special manufacturing.

F. E. BASH.—Nothing has been done to standardize these metals, though I see no reason why something could not be decided upon in that respect. The specific resistance can be varied by varying the amount of manganese in the material, and so far as resistance is concerned we are primarily interested in having the proper temperature coefficient, but the lower the specific resistance, the more wire it is necessary to put on our spool, so that we are also interested in having a high specific resistance. The value that we prefer is 250 ohms per mil foot.

THE CHAIRMAN (W. H. BASSETT, Waterbury Conn.).—Have you investigated any manganin that contained no nickel?

F. E. BASH.—Only in one case; that sample had a very good coefficient. I think that you can get a good coefficient by a number of formulas; we started with values found in some handbooks and experimented with them until we found a good one. As it was very important that we produce the wire in a hurry, we could not take the time to experiment extensively. If we had had the time, we could have gone very much more deeply into the subject, but we carried it just far enough to get a good coefficient and let it go at that.

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Heat Treatment of Aluminum-alloy Castings*

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(Philadelphia Meeting, September, 1919)

IT has been known for a number of years that certain aluminum alloys could be hardened by quenching from a temperature of about 500° C. Immediately after quenching the total increase in hardness is not marked, but the hardness increases gradually so that after about 4 days, it has reached a maximum. The actual increase in hardness probably continues for weeks or even months, but in order to detect the differences after 4 days, it is necessary to make tests at rather long intervals. So far as is known to the authors, Alfred Wilm was the first to discover these properties in aluminum alloys.[1] The aluminum-copper alloys are amenable to this treatment and the addition of magnesium makes the heat-treatment effect more pronounced.

Until recently heat treatment of aluminum alloys has been confined to the worked alloys in the form of sheet or extruded products. The alloy that has been most used in this connection is known commercially as duralumin and has about the following composition: copper not exceeding, 6 per cent.; magnesium not exceeding, 2 per cent.; manganese not exceeding, 1 per cent.; commercial aluminum,[2] balance.

A typically good alloy in this range consists of: copper, 4 per cent.; magnesium, 0.5 per cent.; manganese, 1 per cent.; commercial aluminum, balance. This alloy can be rolled into sheets or extruded; and in this condition it can be heated in the ordinary furnace atmosphere to a temperature near 500° C. and quenched in water. After about 4 days it will have the following physical properties: tensile strength 55,000 to 60,000 lb. per sq. in. (3866 to 4218 kg. per sq. cm.); elongation in 2 in., 15 to 20 per cent. No harmful effects of the furnace gases or even the air, if the heating is effected in an electric furnace in an air atmosphere.

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* A Contribution from Lynite Laboratories of The Aluminum Castings Co.

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[1] Metallographic Investigations of Aluminum Alloys Containing Magnesium. *Metallurgie* (1911) 8, 225.

[2] The commercial aluminum at present available always contains silicon and iron and consequently these elements will be present in the alloy usually not exceeding 0.5 per cent. each.

have been noticed. Also, no deterioration in properties can be detected from the use of water for the quenching medium.

The heat treatment of aluminum-alloy castings presents a problem not found in sheet and extruded products. These products, due to the mechanical working, are practically free from porosity and hence the furnace gases, on the one hand, cannot easily gain access to the interior of the metal and thus produce oxidation within the metal, nor can water, used as a quenching medium, gain access to the interior and cause the ordinary chemical reaction known to take place between water and aluminum, namely, $3H_2O + Al \rightarrow Al(OH)_3 + 3H$. It is true that this reaction is not violent at room temperature nor even in boiling water, but the reaction nevertheless takes place and breaks down the metallic aluminum and, hence, deteriorates the product.

Nearly all aluminum-alloy castings, on the other hand, are more or less porous. The porosity in some castings is not marked at room temperature even when tested under considerable hydraulic pressure. On the other hand, gases, especially at high temperature, permeate these castings with comparative ease. Since these gases are usually oxidizing, the aluminum is oxidized from many microscopic cavities in the interior of the casting. Not only is the oxidation caused in this manner undesirable, but when such a casting is quenched in water, the chemical reaction between water and aluminum further oxidizes the metal.

The result of heating a casting in the ordinary furnace atmosphere and quenching in water varies, therefore, with the degree of soundness of the casting prior to heat treatment. An exceptionally sound casting will receive the maximum benefit, whereas a porous casting will be made worse by heat treatment. As a general tendency, therefore, we may say that of a given group of castings varying in degree of porosity, there will be a greater degree of uniformity of tensile properties before heat treatment than after heat treatment. The relatively non-porous castings will be improved by heat treatment, whereas the more porous will be made worse and thus the uniformity will be impaired. Unless, therefore, a heat-treatment process can be obtained that produces uniform properties, its application to ordinary aluminum-alloy sand castings cannot be of commercial value. Such a process has been worked out. It consists in heating the castings in a bath of fused sodium nitrate and potassium nitrate followed by quenching in oil. This process renders it impossible for excessive oxidation to take place during either heating or quenching.

Results with Water Quenching

A sand casting is usually more porous than a permanent-mold casting and hence we would expect greater non-uniformity in heat-treated sand castings than in heat-treated permanent-mold castings. The following

experiments were reported by G. D. Welty[3] on the heat treatment of permanent-mold castings. The analysis of the alloy was: commercial aluminum, 95.65 per cent.; copper, 3.75 per cent.; manganese, 0.8 per cent.; magnesium, 0.8 per cent.

The treatments were as follows:

Group A—Held at 420° C. for 1 hr. and quenched in water at 20° C.
Group B—Held at 485° C. for 1 hr. and quenched in water at 20° C.
Group C—Held at 520° C. for 1 hr. and quenched in water at 20° C.
Group D—Held at 620° C. for 15 min. and quenched in water at 20° C.
Group E—Held at 620° C. for 15 min. and quenched in water at 20° C. then reheated to 350° C. for 1 hr. and quenched in water at 20° C.

The original castings were in the form of 3-in. (7.6-cm.) shrapnel fuse bodies, from which test bars 0.210 in. (5.5 mm.) diameter and ¾ in. (19 mm.) between punch marks, were machined. The results are given in Tables 1, 2, and 3. Groups D and E were so badly flawed from high-temperature quenching as to make tensile tests worthless.

TABLE 1.—*Results of Tests on Samples in Group A*

Bar No.	Ultimate Strength, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Per Cent., Elongation	Bar No.	Ultimate Strength, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Per Cent., Elongation
1	32,000	26,800	2.7	5	32,700	26,900	2.7
2	28,800	25,850	2.7	6	34,200	27,700	2.7
3	34,600	25,600	2.7	7	32,300	26,200	2.7
4	30,350	27,000	2.7	8	32,800	26,000	2.7

TABLE 2.—*Group B.*

Bar No.	Ultimate Strength, Lb. per Sq. In.	Per Cent., Elongation
1	34,350	2.7
2	29,400	2.7
3	41,800	2.7
4	28,800	2.7
5	41,300	2.7
6	21,700	2.7
7	25,800	2.7
8	32,500	2.7

TABLE 3.—*Group C.*

Bar No.	Ultimate Strength, Lb. per Sq. In.	Per Cent., Elongation
1	38,000	0
2	41,800	0
3	32,000	0
4	37,000	0
5	47,000	0
6	35,600	0
7	42,700	0
8	43,000	0

It will be noted that the samples quenched from 420° C., namely, Group A, were quite uniform but the tensile strength was not increased ot any great extent. The castings, before heat treatment, would average

[3] Thesis, Case School of Applied Science, May, 1917.

about the same as Group A. The samples in Group B were very erratic while those in C are about as uniform as could be expected, with the exception of bar 3. The samples were all heated in an electric furnace in the furnace atmosphere, which in this case was ordinary air.

Table 4 gives the results of tensile tests on sand-cast test bars of an alloy containing: commercial aluminum, 91.55 per cent.; copper, 8 per cent.; iron, 0.3 per cent.; magnesium, 0.25 per cent. These bars were heated in an electric furnace at 500° C. in air atmosphere for 1 hr. and

TABLE 4.—*Results of Tensile Tests on Sand-cast Bars*

Bar No.	Break Stress, Lb. per Sq. In.	Bar No.	Break Stress, Lb. per Sq. In.	Bar No.	Break Stress, Lb. per Sq. In.
1	17,720	8	32,100	15	27,600
2	24,450	9	26,950	16	30,750
3	24,400	10	25,900	17	21,450
4	36,400	11	34,050	18	29,800
5	16,600	12	21,600	19	21,250
6	21,250	13	23,300	20	26,600
7.	25,200	14	18,700		

quenched in water. The tensile results vary from 34,050 lb. per sq. in. to 16,600 lb. per sq. in. (2400 kg. per sq. cm. to 1167 kg. per sq. cm.), and the average was 25,303 lb. per sq. in. (1778 kg. per sq. cm.). The average of ten bars without heat treatment was 25,500 lb. per sq. in., the minimum being 24,000 lb. per sq. in. and the maximum 28,000 lb. per sq. in. It will thus be seen that the average was slightly lowered by heat treatment and the maximum was increased and the minimum was decreased. With this particular treatment, therefore, the castings would have been less uniform after heat treatment than before.

Table 5 gives the results of sand-cast test bars of Sample 916. The analysis of this heat was as follows: commerical aluminum, 94.5 per cent.; copper, 4.5 per cent.; iron, 1 per cent. All the remaining test bars reported in this paper were cast in green sand in the form recommended by the American Society for Testing Materials—0.505 in. (12.8 cm.) in diameter with 2 in. (5 cm.) between punch marks. The ends of the bars were threaded before testing, but the test portions of the bars were not machined. The bars were heated to 500° C. for 1 hr. in a niter bath, quenched in boiling water, and left in the boiling water for 1 hour.

Tables 6, 7, and 8 give the results of heat treatment of test bars from the same lot as Table 5 after heating for 1 hr. in a bath of niter and quenching in fish oil. Table 6 gives the results of quenching in fish oil and heating for 1 hr. at 100° C. in Crisco. Table 7 gives the results of heating for 1 hr. at 150° C. in Crisco after quenching in fish oil. Table 8 gives

TABLE 5

Bar No.	Yield Stress, Lb. per Sq. In.	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
1	5042	20,420	2.0
2	6322	19,950	2.0
3	7340	25,500	5.0
4	6920	27,100	5.5
5	7250	26,100	6.5
6	6930	25,200	6.0
7	6930	24,900	5.5
8	6570	22,700	5.25
9	7180	26,000	5.5
10	6580	23,800	4.75
11	6940	25,300	6.0
12	6780	24,100	4.0
Average.	6730	24,250	4.8

TABLE 6

Bar No.	Yield Stress, Lb. per Sq. In.	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
1	5480	26,130	6.5
2	5740	23,800	5.0
3	6000	25,500	6.0
4	6690	25,400	6.5
5	6590	27,400	5.5
6	6450	25,800	6.0
7	6655	25,710	6.0
8	6542	24,180	4.0
9	6500	25,500	5.5
10	7150	25,780	
11	6700	24,820	5.5
12	6346	23,540	4.35
Average.	6400	24,984	5.1

results of heating for 1 hr. at 200° C. in Crisco after quenching in fish oil. Table 9 gives the tensile properties of sand-cast test bars of the same lot as Tables 5, 6, 7, and 8, as cast.

The idea of quenching the samples in boiling water and leaving in boiling water for 1 hr. was first communicated to the writers by Dr. E. Blough of the Aluminum Co. of America, New Kensington, Pa. The

TABLE 7

Bar No.	Yield Stress, Lb. per Sq. In.	Break Stress, Lb. per Sq. In.	Per Cent. Elongation
1	6798	25,440	6.0
2	6230	24,240	4.5
3	6570	24,280	5.5
4	6500	24,930	5.5
5	6970	25,620	6.0
6	6550	24,640	6.0
7	6560	24,150	5.5
8	6930	25,650	6.0
9	6300	24,680	5.5
10	6350	24,000	6.0
11	6290	24,200	4.5
12	6290	24,200	5.0
Average..	6529	24,669	5.5

TABLE 8

Bar No.	Yield Stress, Lb. per Sq. In.	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
1	5720	24,700	5.5
2	5720	25,800	6.0
3	5870	25,900	6.5
4	5940	25,510	5.8
5	5500	24,920	5.0
6	5760	25,710	6.5
7	5780	26,000	6.75
8	5185	23,700	5.25
9	5500	23,980	4.5
10	5670	24,590	6.5
11	5940	24,410	5.0
12	6010	24,580	5.5
Average..	5700	25,370	5.5

TABLE 9

Bar No.	Yield Point, Lb. per Sq. In.	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
1	5918	22,820	4.0
2	6000	22,600	4.0
3	6020	22,900	4.6
4	6519	23,720	6.0
5	6740	23,250	3.5
6	6780	22,980	4.0
7	6710	22,300	4.25
8	6810	23,730	5.75
9	7060	25,120	5.5
10	6399	22,110	4.0
11	6590	22,500	4.5
12	6410	22,030	4.5
Average.....	6501	23,005	4.60

TABLE 10.—*Numbers and Analysis of Samples*

Bar No.	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.	Aluminum by Difference, Per Cent.
910	2.84	0.36	0.23	Balance
911	2.99	1.16	0.21	Balance
912	3.15	1.10	0.24	Balance
913	3.36	1.64	0.26	Balance
914	4.07	0.42	0.24	Balance
915	4.15	0.60	0.60	Balance
916	4.5	1.43	0.35	Balance
917	4.3	2.7	0.22	Balance
918	4.88	0.38	0.24	Balance
919	5.18	0.81	0.29	Balance
920	5.42	1.39	0.25	Balance
921	5.5	1.58	0.31	Balance
922	6.0	0.39	0.26	Balance
923	6.24	0.68	0.21	Balance
924	6.20	1.33	0.27	Balance
925	6.17	1.86	0.31	Balance
955	7.47	0.38	0.31	Balance
962	7.72	0.88	0.30	Balance
970	8.56	0.83	0.35	

object is to hasten the aging effect. The aging for 1 hr. at 100° C. is about as effective as aging for 4 days at room temperature; higher temperatures than 100° C. will effect aging more quickly. The quantitative

TABLE 11

	Bar No.	Average Break Stress	Average Per Cent. Elongation	Maximum		Minimum	
				Break Stress	Per Cent. Elongation	Break Stress	Per Cent. Elongation
As cast	910	16,837	4.4	17,300	6.5	16,040	3.0
Heat treated	910	22,880	5.0	25,930	6.0	22,600	4.0
As cast	911	20,150	6.3	22,270	7.0	12,230	5.5
Heat treated	911	23,850	7.3	25,010	8.0	22,550	6.5
As cast	912	22,362	6.2	24,660	7.8	19,700	4.5
Heat treated	912	25,274	7:0	25,680	7.8	24,930	6.5
As cast	913	24,060	5.8	24,680	6.5	23,410	5.0
Heat treated	913	22,792	5.9	24,730	8.5	17,520	2.0
As cast	914	15,640	2.5	16,220	2.5	15,210	2.5
Heat treated	914	20,242	3.8	21,700	4.0	17,860	3.0
As cast	915	17,358	3.3	18,810	4.0	15,080	3.0
Heat treated	915	22,514	3.8	23,990	4.5	21,020	3.5
As cast	916	23,005	4.6	25,120	6.0	22,030	3.5
Heat treated	916	24,669	5.5	25,650	6.0	24,000	4.5
As cast	917	21,856	4.4	22,950	5.5	21,250	3.5
Heat treated	917	24,888	5.1	25,680	6.0	23,350	4.5
As cast	918	17,866	2.6	18,570	3.0	16,670	2.5
Heat treated	918	20,641	1.9	23,650	3.3	18,750	1.0
As cast	919	19,307	3.0	19,730	3.0	18,850	3.0
Heat treated	919	24,990	4.1	26,890	5.0	23,650	3.5
As cast	920	20,103	3.3	21,110	4.0	19,600	3.0
Heat treated	920	25,015	3.5	27,380	5.0	22,200	3.0
As cast	921	19,606	2.9	20,820	3.0	18,820	2.5
Heat treated	921	26,091	2.9	28,600	3.0	23,660	2.5
As cast	922	23,188	3.3	25,350	3.5	21,200	2.5
Heat treated	922	25,500	3.9	26,900	5.0	24,050	3.5
As cast	923	19,438	2.2	20,020	2.3	19,020	2.0
Heat treated	923	25,710	2.3	27,500	2.5	24,200	1.3
As cast	924	20,776	2.4	21,700	3.0	18,100	2.0
Heat treated	924	27,768	2.3	29,610	2.5	22,930	1.5
As cast	925	22,486	2.6	23,300	3.0	21,820	2.5
Heat treated	925	25,016	3.4	25,910	4.0	23,050	3.0
As cast	955	19,582	1.6	20,990	2.5	17,920	1.3
Heat treated	955	23,066	2.7	24,800	3.0	20,210	1.0
As cast	962	21,181	1.3	21,840	1.5	20,050	1.0
Heat treated	962	25,562	1.3	26,210	1.8	24,700	0.5
As cast	970	25,619	0.7	27,770	1.0	24,320	0.5
Heat treated	970	28,383	1.1	29,020	1.5	27,780	0.5

effect of these temperatures has recently been treated by Merica[4] and others.

[4] P. D. Merica, R. G. Waltenberg, and H. Scott: Heat Treatment and Constitution of Duralumin, this volume.

Tables 5 to 9 show that heating in a bath of niter and quenching in oil gives uniform results. Not only are the results uniform, but an increase in tensile strength and elongation is effected. The increase in this particular alloy is not very marked, but the results given below will indicate the degree of improvement in alloys of a different chemical composition.

A series of alloys was made up not only to test the amenability to heat treatment, but to test the properties of the alloys themselves in the cast condition. To conserve space, the average tensile strength of five bars is recorded and a maximum and minimum indicated to show the degree of uniformity. Table 10 gives the list of samples, together with the chemical analysis.

Table 11 shows the physical properties of these alloys, together with the effect of heat treatment. In all cases samples were heated for 1 hr. in a bath of niter and quenched in fish oil and then heated for 1 hr. at a temperature of 150° C. in Crsico.

From the results given in Table 11, it is evident that the particular heat treatment used not only improved the desirable properties of these alloys, but the degree of uniformity in the heat-treated bars is sufficient for commercial product. In many cases the heat-treated bars show more uniform results than the bars as cast. Note particularly Samples 911, 912, 915, 916, 922, 925, and 970.

TABLE 12.—*Numbers and Analysis of Samples*

Bar No.	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.	Magnesium, Per Cent.	Aluminum, by Difference, Per Cent.
983	6.26	0.41	0.33	.....	Balance
984	6.03	0.85	0.33	.....	Balance
985	5.72	1.29	0.30	.....	Balance
986	2.94	1.22	0.31	.....	Balance
987	3.07	1.25	0.32	0.125	Balance
988	2.97	1.26	0.36	0.25	Balance
989	3.33	1.32	0.38	0.50	Balance
990	4.88	0.83	0.30	.....	Balance
991	4.65	0.84	0.33	0.05	Balance
992	4.99	0.85	0.29	0.10	Balance
993	4.57	0.84	0.29	0.20	Balance

EFFECT OF VARYING MAGNESIUM, COPPER, AND IRON ON HEAT TREATMENT OF ALUMINUM ALLOYS

Table 12 shows the composition of the alloys used. Table 13 shows the physical properties of these alloys, together with the relation between the properties of the cast and heat-treated samples. Tables 14 and 15 show the analysis and results respectively when copper and iron are maintained approximately constant and magnesium is varied up to 1.6 per cent.

TABLE 13

	Bar No.	Average Break Stress, Lb. per Sq. In.	Average Per Cent., Elongation	Maximum		Minimum	
				Break Stress, Lb. per Sq. In.	Per Cent., Elongation	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
As cast	983	21,310	2.3	22,550	3.0	19,760	2.0
Heat treated	983	25,819	1.8	27,000	2.5	24,490	1.5
As cast	984	20,104	2.5	20,350	3.0	19,340	2.0
Heat treated	984	25,406	2.3	26,290	3.0	24,380	2.0
As cast	985	22,029	2.4	22,520	2.8	21,400	2.0
Heat treated	985	27,539	2.9	28,870	3.5	26,300	2.5
As cast	986	23,864	7.0	24,500	8.0	22,170	5.5
Heat treated	986	24,698	7.7	25,400	9.0	23,680	6.5
As cast	987	25,595	3.18	28,000	3.5	22,650	2.0
Heat treated	987	28,459	3.9	30,060	5.5	21,000	1.5
As cast	988	25,883	2.9	28,300	3.5	22,940	1.5
Heat treated	988	28,743	2.9	29,820	4.0	24,290	1.0
As cast	989	27,643	2.4	28,800	2.8	25,550	2.0
Heat treated	989	35,107	2.3	36,400	2.8	33,790	2.0
As cast	990	18,699	2.7	19,510	3.5	17,700	2.0
Heat treated	990	23,946	2.8	26,080	3.5	22,410	2.0
As cast	991	21,196	1.8	22,100	2.5	20,250	1.5
Heat treated	991	27,057	2.2	28,250	2.8	26,000	1.5
As cast	992	21,846	1.0	22,680	1.5	21,050	0.8
Heat treated	992	26,015	2.1	27,450	2.8	24,880	1.5
As cast	993	22,508	1.3	23,670	1.5	21,900	1.0
Heat treated	993	27,380	1.9	28,410	2.5	26,610	1.5

TABLE 14.—*Analysis of Samples When Magnesium is Varied*

Bar No.	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.	Magnesium, Per Cent.	Aluminum, by Difference, Per Cent.
985	5.72	1.29	0.30	0	Balance
1028	3.49	1.37	0.34	0.10	Balance
1029	3.32	1.45	0.34	0.20	Balance
1030	3.18	1.37	0.36	0.30	Balance
1031	3.12	1.38	0.26	0.40	Balance
1032	3.03	1.43	0.29	0.50	Balance
1033	3.33?	1.40	0.31	0.60	Balance
1034	3.42?	1.47	0.35	0.70	Balance
1035	3.15	1.45	0.31	0.80	Balance
	Added	Added		Added	Added commercial aluminum
1091	3	1		1.0	Balance
1092	3	1		1.2	Balance
1093	3	1		1.4	Balance
1094	3	1		1.6	Balance

TABLE 15.—*Results of Tests When Magnesium is Varied*

	Bar No.	Average Break Stress, Lb. per Sq. In.	Average Per Cent., Elongation	Maximum		Minimum	
				Break Stress, Lb. per Sq. In.	Per Cent., Elongation	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
As cast	985	22,029	2.4	22,520	2.8	21,400.	2.0
Heat treated	985	27,539	2.9	28,870	3.5	26,300	2.5
As cast	1028	27,231	4.1	28,660	4.5	26,610	3.0
Heat treated	1028	27,373	5.6	28,200	6.5	26,660	5.0
As cast	1029	27,620	3.7	28,900	4.0	26,700	3.3
Heat treated	1029	28,890	5.2	30,120	6.0	28,170	5.0
As cast	1030	27,170	3.0	27,600	3.0	26,800	3.0
Heat treated	1030	30,440	5.4	31,270	5.5	29,530	5.4
As cast	1031	27,568	3.0	28,070	3.0	27,000	3.0
Heat treated	1031	31,964	3.9	34,450	4.5	29,170	3.0
As cast	1032	26,790	2.8	28,100	3.5	26,350	2.5
Heat treated	1032	33,180	2.8	33,600	3.0	31,950	2.5
As cast	1033	27,090	2.0	28,870	2.0	26,200	1.5
Heat treated	1033	33,738	2.7	34,540	3.0	32,850	2.0
As cast	1034	28,400	2.1	29,200	3.0	26,500	1.5
Heat treated	1034	34,784	2.5	35,980	2.5	33,460	2.5
As cast	1035	28,848	2.2	29,810	2.5	27,160	2.0
Heat treated	1035	36,330	2.3	37,350	2.8	34,510	1.5
As cast	1091	29,750	1.2	32,100	1.5	28,100	1.0
Heat treated	1091	36,676	1.2	37,400	1.5	36,250	1.0
As cast	1092	29,650	1.2	30,600	1.5	28,700	1.0
Heat treated	1092	37,840	1.4	39,840	1.5	36,900	1.5
As cast	1093	28,995	1.3	30,630	1.5	27,450	1.0
Heat treated	1093	36,103	1.0	37,650	1.0	34,810	1.0
As cast	1094	28,829	1.0	30,120	1.0	27,900	1.0
Heat treated	1094	35,956	1.3	38,320	1.5	31,900	0.5

NOTES ON THE GRAPHS

The more important results given in the last several tables are summarized in the graphs shown in Figs. 1 to 7 inclusive. Fig. 1 shows the effect of variation of iron with copper approximately constant at 6 per cent. The tensile strength and elongation show minima in the untreated samples between 0.7 and 1.3 per cent. iron. This minimum does not occur in the tensile strength of the heat-treated samples.

Fig. 2 shows the effect of varying iron with copper constant at about 3 per cent. The tensile strength and elongation in both the heat-treated and the untreated samples increase with increase in iron, the best properties occurring at about 1 per cent. iron. These results indicate that the addition of iron is more beneficial to aluminum alloys low in copper than those high in copper.

Fig. 3 shows the effect of variation of copper on an aluminum alloy containing 0.7 per cent. iron. The tensile strength and elongation show minima at about 4 per cent. copper, except in the elongation of the

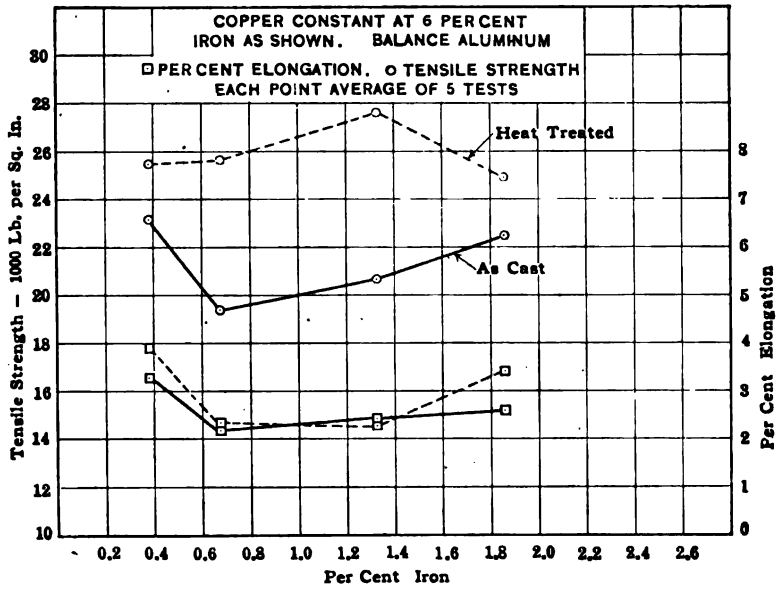


FIG. 1.—EFFECT OF VARIATION IN IRON CONTENT AND HEAT TREATMENT ON STRENGTH AND ELONGATION ON CAST ALUMINUM ALLOY CONTAINING 6 PER CENT. COPPER.

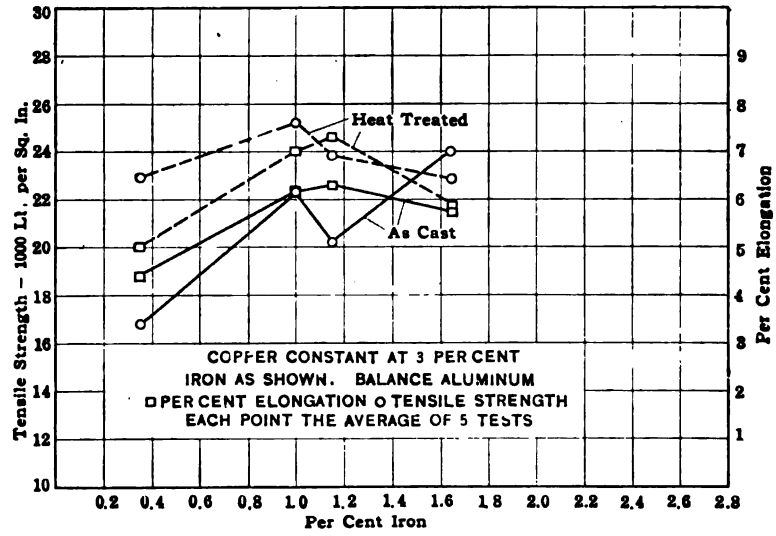


FIG. 2.—EFFECT OF VARIATION IN IRON CONTENT AND HEAT TREATMENT ON CAST ALUMINUM ALLOY CONTAINING 3 PER CENT. COPPER.

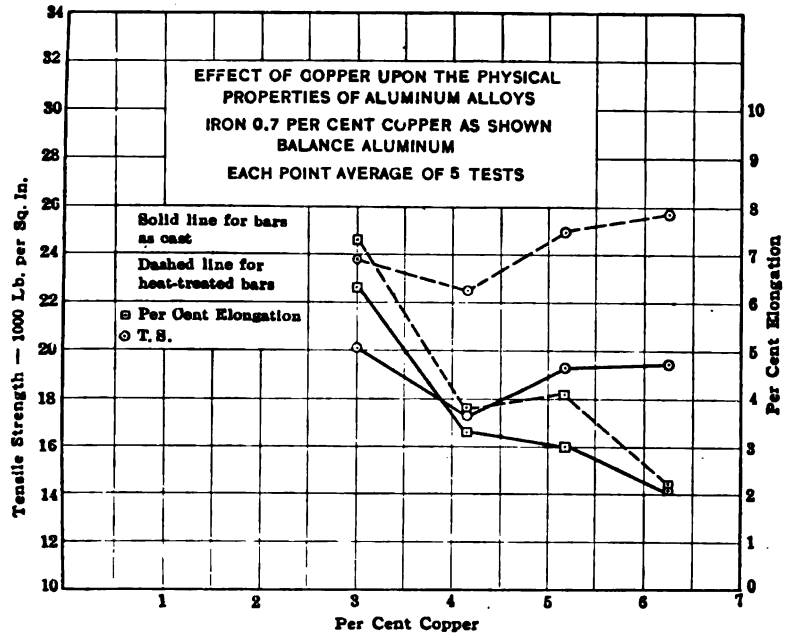


FIG. 3.—EFFECT OF VARIATION IN COPPER CONTENT AND HEAT TREATMENT ON CAST ALUMINUM ALLOY CONTAINING 0.7 PER CENT.

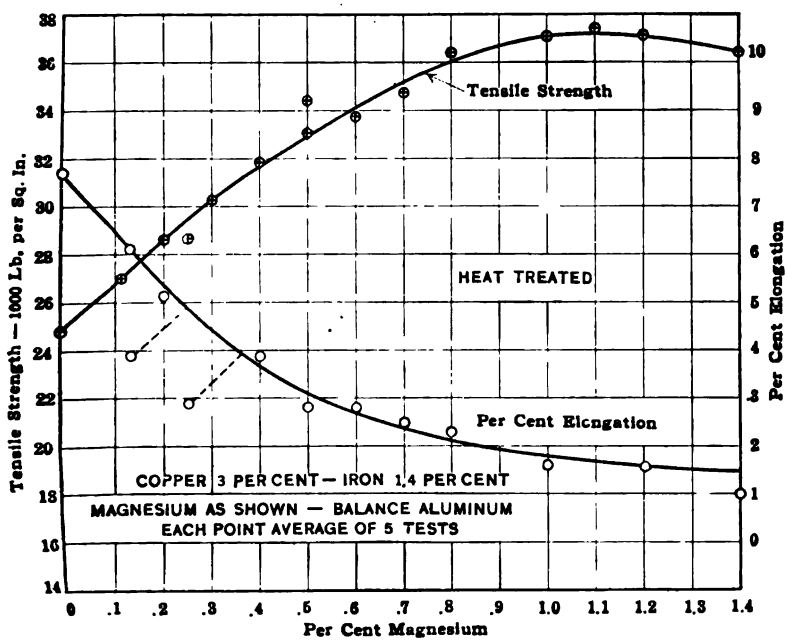


FIG. 4.—EFFECT OF VARIATION IN MAGNESIUM CONTENT AND HEAT TREATMENT ON CAST ALUMINUM ALLOY CONTAINING 3 PER CENT. COPPER AND 1.4 PER CENT. IRON.

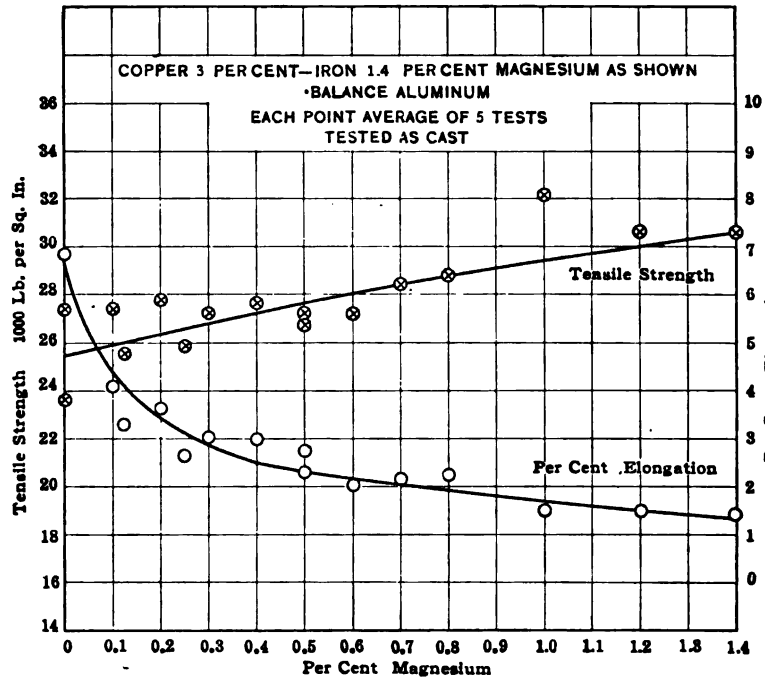
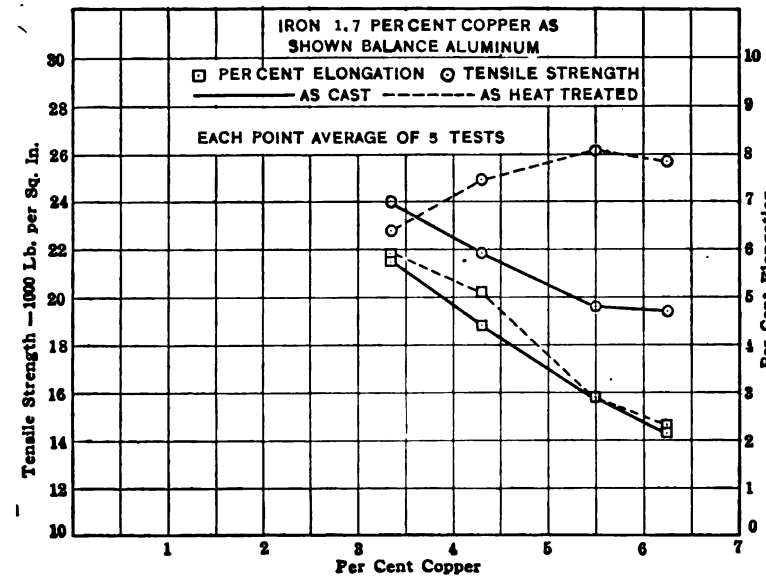


FIG. 5.—EFFECT OF VARIATION IN MAGNESIUM CONTENT ON CAST ALUMINUM ALLOY CONTAINING 3 PER CENT. COPPER AND 1.4 PER CENT. IRON.



IG. 6.—EFFECT OF VARIATION IN COPPER CONTENT AND HEAT TREATMENT ON CAST ALUMINUM ALLOY CONTAINING 1.7 PER CENT. IRON.

untreated samples, in which a discontinuity is suggested. (Compare this graph with Fig. 7.)

Fig. 4 shows the effect of magnesium and heat treatment on an aluminum alloy containing 3 per cent. copper and 1.4 per cent. iron. The tensile strength increases up to about 1.1 per cent. magnesium after which it decreases and the elongation decreases continuously as the magnesium content increases.

Fig. 5 shows the effect of variation of magnesium on an alloy containing 3 per cent. copper and 1.4 per cent. iron. The samples are the same as those shown in Fig. 4 except that the results given in Fig. 5 were obtained on untreated test bars. In general, the tensile strength

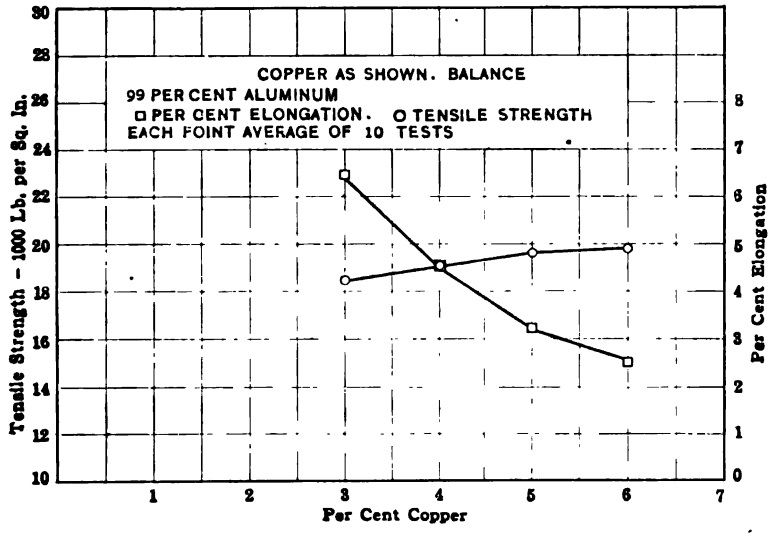


FIG. 7.—EFFECT OF VARIATION IN COPPER CONTENT ON COMMERCIAL 99 PER CENT. ALUMINUM.

increases with increase in magnesium content although a maximum was observed at 1 per cent. magnesium. The elongation decreases continuously as the magnesium content increases. The results shown in Fig. 5 are less uniform than those in Fig. 4. We suggest as a reason for this that the rate of cooling after heat treatment was very much more uniform than the rate of cooling test bars after casting. Since the properties vary with the rate of cooling, the more uniform rate should produce more uniform results. The effect of heat treatment has been to increase tensile strength in all of the samples and to increase the elongation in all samples containing less than 1 per cent. magnesium.

Fig. 6 shows the effect of variation in copper content with iron approximately constant at 1.7 per cent. The tensile strength and elongation of the untreated bars decreases with increased copper content, whereas,

in the heat-treated bars the tensile strength increases and elongation decreases with increased copper content. With iron constant at 1.7 per cent., heat treatment is very much more beneficial with 6 per cent. copper than with 3 per cent. copper.

Fig. 7 shows the effect of variation of copper on the tensile strength and elongation of aluminum alloy castings. The tensile strength rises gradually from 3 per cent. to 6 per cent. copper and the elongation falls off rapidly.

Effect of Several Heat Treatments

The double heat treatment to which steel is sometimes subjected prompted us to try the effect of several heat treatments on an aluminum alloy containing: copper, 3.0 per cent.; iron, 1.0 per cent.; magnesium, 0.5 per cent.; commercial 99 per cent. aluminum, balance. Twenty-five sand-cast test bars were made from one heat and divided into five lots of five each. One set of five was tested as cast; the second set was given a normal heat treatment, that is, the bars were heated in niter at 500° C. for 1 hr., quenched in oil, and then reheated to 150° C. for 1 hr. The third, fourth, and fifth sets were given two, three, and four similar heat treatments, respectively, and then tested. The results are shown in Table 16. These results show that there is no particular advantage in heat treating these alloys more than once, but that four heat treatments and probably more, can be used without harming the product.

Table 16.—*Results of Increasing Number of Heat Treatments*

Treatment	Average Break Stress, Lb. per Sq. In.	Average Per Cent., Elongation	Maximum		Minimum	
			Break Stress, Lb. per Sq. In.	Per Cent., Elongation	Break Stress, Lb. per Sq. In.	Per Cent., Elongation
As cast	28,668	3.5	30,300	4.5	27,350	3.0
One heat treatment	29,612	3.6	30,860	4.0	29,040	3.0
Two heat treatments	30,866	4.4	31,420	5.0	29,520	3.0
Three heat treatments	31,010	3.0	32,500	4.5	28,750	2.5
Four heat treatments	29,924	3.4	31,000	4.0	28,420	2.5

Effect of Heat Treatment on Microscopic Structure

Improvement in the properties of aluminum alloys by heat treatment is dependent on the solubility of certain components, particularly $CuAl_2$, in the aluminum in the solid state just below the melting point, and the tendency on slow cooling for these dissolved components to be thrown out of solution. The paper by Dr. P. D. Merica, *et al*, previously referred to, discusses this phase of the subject in detail. Rapid cooling

from a high temperature prevents the precipitation of some of these dissolved substances into relatively large masses and hence the physical properties are different from the slowly cooled samples.

Fig. 8 is a micrograph of sample 910 as cast. Fig. 9 is a micrograph at the same magnification of this sample after heat treatment. The particular test bar from which the micrograph in Fig. 8 was taken had a

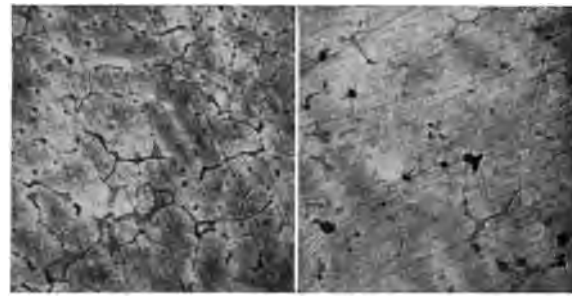


FIG. 8. FIG. 9.

FIG. 8.—ALUMINUM-ALLOY CASTING CONTAINING 2.84 COPPER AND 0.36 IRON, AS CAST. × 50. DILUTE HNO_3.

FIG. 9.—ALUMINUM-ALLOY CASTING CONTAINING 2.84 COPPER AND 0.36 IRON, HEAT TREATED. × 50. DILUTE HNO_3.

tensile strength of 16,960 lb. per sq. in. (1192 kg. per sq. cm.) and an elongation of 3.5 per cent. while the tensile strength of that shown in Fig. 9 was 22,600 lb. per sq. in., and the elongation was 6 per cent. The chemical analysis is given in Table 10. It will be noted that the quantity

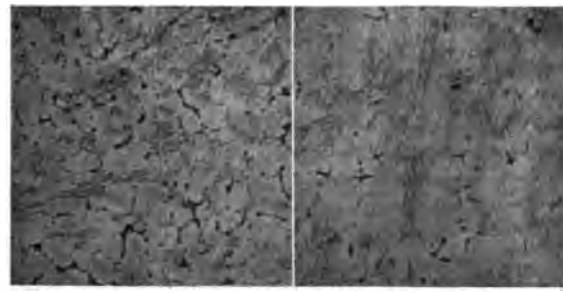


FIG. 10. FIG. 11.

FIG. 10.—ALUMINUM-ALLOY CASTING CONTAINING 6 PER CENT. COPPER AND 0.39 PER CENT. IRON, AS CAST. × 50. DILUTE HNO_3.

FIG. 11.—ALUMINUM-ALLOY CASTING CONTAINING 6 PER CENT. COPPER AND 0.39 PER CENT. IRON, HEAT TREATED. × 50. DILUTE HNO_3.

of the network substance ($CuAl_2$) is very much greater in Fig. 8 than in Fig. 9, and hence the heat-treated sample more nearly approaches a solid-solution structure.

Fig. 10 is a micrograph of sample 922, containing 6 per cent. copper, in the unheat-treated condition; Fig. 11 is a micrograph of the same

sample after heat treatment. It will be noted that the amount of network material in Fig. 10 is greater than in Fig. 8, due to the higher copper content of the former, but that the amount of network material is less in Fig. 11 than in Fig. 10, due to heat treatment.

Fig. 12 is a micrograph of sample 925, the composition of which is shown in Table 10. This bar was not heat treated. The iron content

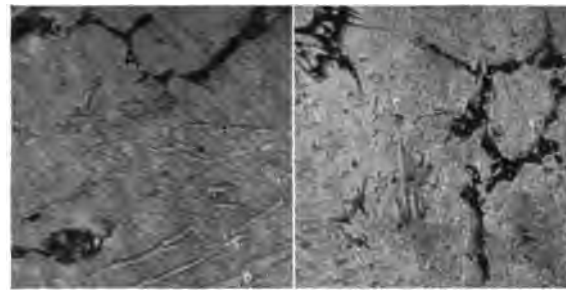


FIG. 12. FIG. 13.

FIG. 12.—ALUMINUM-ALLOY CASTING CONTAINING 6.17 PER CENT. COPPER AND 1.86 PER CENT. IRON, AS CAST. × 125. DILUTE HNO_3.

FIG. 13.—ALUMINUM-ALLOY CASTING CONTAINING 6.17 PER CENT. COPPER AND 1.86 PER CENT. IRON, HEAT TREATED. × 125. DILUTE HNO_3.

was high, consequently many needles of $FeAl_3$ are present. Fig. 13 is a micrograph of the same sample after heat treatment. It will be noted that the white needles of $FeAl_3$ appear to have been unaffected by the heat treatment.

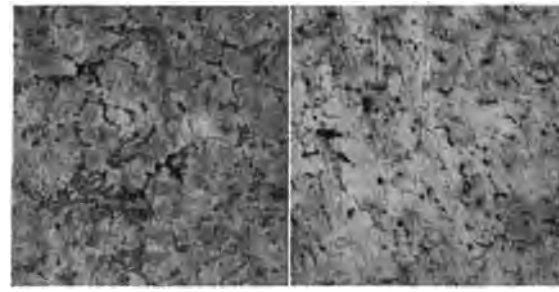


FIG. 14. FIG. 15.

FIG. 14.—ALUMINUM-ALLOY CASTING CONTAINING 2.83 PER CENT. COPPER AND 1.58 PER CENT. IRON, AS CAST. × 50. DILUTE HF.

FIG. 15.—ALUMINUM-ALLOY CASTING CONTAINING 2.83 PER CENT. COPPER AND 1.58 PER CENT. IRON, HEAT TREATED. × 50. CONC. HF.

Fig. 14 is a micrograph of an aluminum alloy containing 2.83 per cent. copper, 1.58 per cent. iron, 0.32 per cent. silicon, and balance commercial 99 per cent. aluminum, in the untreated condition. Fig. 15 is a micrograph of the same sample heat-treated. Owing to the high

iron content and relatively low copper content, the difference in structure in these two samples is not marked.

It has been observed frequently that aluminum castings containing copper have two distinct structure systems. There is a system of primary grains that have apparently formed from the liquid state in the form of a solid solution. These grains are usually so large that they can be seen with the naked eye after deep etching and can be observed without difficulty by means of a 20*X* pocket glass or a low-power microscope. They are divided, as usual, into grains of different tints, each whole grain having a substantially uniform tint, but different from that of its neighbors. Fig. 16 shows this condition in sample 921 as cast; the analysis of this sample is given in Table 10. Fig. 17 shows the structure of the same sample after heat treatment. The large grains of primary solid solution can be seen in Fig. 17 with dark and light tints. Inside

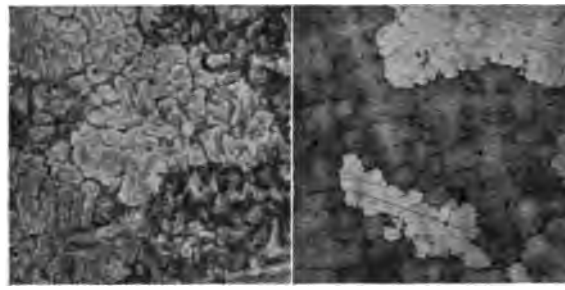


FIG. 16. FIG. 17.

FIG. 16.—ALUMINUM-ALLOY CASTING CONTAINING 5.5 PER CENT. COPPER AND 1.58 PER CENT. IRON, AS CAST. × 37.5. CONC. HF + CONC. HNO_3.

FIG. 17.—ALUMINUM-ALLOY CASTING CONTAINING 5.5 PER CENT. COPPER AND 1.58 PER CENT. IRON, HEAT TREATED. × 37.5. CONC. HF + CONC. HNO_3.

of these large grains there is a well-developed network of $CuAl_2$, which has not interfered with the original orientation of the grains. This indicates that the expulsion of the $CuAl_2$ molecules from the solid solution has taken place after solidification without substantial disruption of the original orientation of the grains as a whole. The contrast in the original grains is very much more marked in the heat-treated samples than in the untreated samples.

EFFECT OF HEAT TREATMENT ON IMPACT

Eight bars of an alloy containing 3 per cent. copper, 1 per cent. iron, 0.5 per cent. magnesium and balance commercial 99 per cent. aluminum, were cast from one heat and four were tested for impact, as cast, in an Izod machine and four were heat-treated and tested with results shown in Table 17. It will be noted that heat-treatment increased the average impact values more than 30 per cent.

TABLE 17.—*Effect of Heat Treatment on Impact*

Sample	Treatment	Ft.-lb.	Sample	Treatment	Ft.-lb.
1	As cast	2.0	H-1	Heat treated	2.7
2	As cast	1.7	H-2	Heat treated	2.6
3	As cast	1.6	H-3	Heat treated	2.0
4	As cast	2.3	H-4	Heat treated	3.0
Average.....	.....	1.9	Average....	.....	2.6

SUMMARY

The heat treatment of the rolled and extruded aluminum alloy is first described briefly. The heat-treating process consists essentially in heating to a temperature near 500° C. and quenching in water. The properties change at room temperature after quenching, the maximum aging effect being completed for practical purposes in 4 days.

It is shown that heating aluminum-alloy castings in the ordinary furnace atmosphere and then quenching in water does not produce uniform results.

It is suggested that the non-uniform results are due to porosity in the castings and that heating in the furnace atmosphere followed by quenching in water oxidizes the casting from many small holes in the interior. Also the temperature is under better control in the niter bath.

A method of heat treatment that gives uniform results in castings is described. This heat treatment has for its object the elimination of the atmosphere and quenching medium which could permeate and oxidize the interior of the porous castings. Good results have been obtained by heating in a bath of fused niter followed by quenching in oil.

Results of many heat-treatment tests on cast alloys of various compositions are tabulated; they are summarized in the graphs shown in Figs. 1 to 7 inclusive.

It is shown that in general, the heat treatment increases both tensile strength and elongation of the aluminum-alloy castings. The amount of increase in tensile strength varies from 0 to 40 per cent. and the increase in elongation varies from 0 to 100 per cent. In a few isolated instances the tensile strength was slightly lowered by heat treatment but in the same samples the elongation was increased. Also in a few isolated instances the elongation was decreased but in these cases the strength was increased considerably.

The effect of heat treatment on the structure of aluminum-alloy castings is shown by micrographs in Figs. 8 to 17, inclusive. It is shown that: The higher the copper content, the greater is the quantity of network of $CuAl_2$; the greater the quantity of iron, the more needles of

$FeAl_3$. The heat-treated samples show less $CuAl_2$ than the untreated samples.

Results are given indicating that two heat treatments do not improve the castings much more than a single treatment and four treatments can be applied without harmful results.

A table showing the effect of heat treatment on impact resistance is given, indicating that heat-treated aluminum-alloy cast bars containing 3 per cent. copper, 1 per cent. iron, and 0.5 per cent. magnesium have about 30 per cent. greater resistance to impact than cast bars of the same alloy without treatment.

DISCUSSION

G. K. BURGESS,* Washington, D. C.—At the Bureau of Standards it was decided, in order to study the high-aluminum end of these curves, that efforts should be made to prepare pure aluminum, and the promise of getting aluminum practically free from the two elements that have such great effect in very small quantities, namely, silicon and iron, and which practically always occur with the aluminum, is very good. We are hoping that within a reasonable time we will have aluminum practically free from these elements.

PAUL D. MERICA, Bayonne, N. J.—In a recent article before the American Society for Testing Materials,[5] I ventured the prediction that the heat treatment of light alloy castings of aluminum containing copper would have commercial possibilities owing to the marked improvement in the mechanical properties of these alloys produced by it. I am glad to find this opinion confirmed by the results of the tests that the authors have just presented. These agree essentially with those of the above article and show that an increase of from 0 to 50 per cent. in tensile strength together with an increase of from 0 to 100 per cent. in elongation may be obtained by heating such alloys to 500° C., quenching in oil, and aging for some time either at ordinary temperatures or at about 100° C. It is hardly necessary to point out the advantages for various purposes of these improved mechanical properties.

At the time of carrying out my tests I was somewhat in doubt whether castings of complicated shape could successfully be quenched from 500° without cracking and, therefore, subjected the specimens to the less drastic treatment of heating to 500°, cooling in air, and aging. This treatment gave results not markedly inferior to those shown by the

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* Chief, Division of Metallurgy, U. S. Bureau of Standards.

[5] P. D. Merica and C. P. Karr: Some Tests of Light Aluminum Casting Alloys; Effect of Heat Treatment. *Proc.* Am. Soc. Test. Mat. (1919).

authors, as far as tensile strength improvement is concerned, but much less uniform in respect to elongation. This, however, I am now inclined to attribute, following the authors' suggestion, to poor heating conditions allowing internal oxidation. I should be interested to know the authors' opinion as to whether small commercial castings could withstand without cracking or warping the rather drastic heat treatment they have adopted. If this should not be the case I believe that the application of their method of heating in niter, to prevent oxidation in conjunction with air-cooling and aging, might give results as good as those produced by quenching.

The decrease in the visible amount of free $CuAl_2$ in the alloys produced by the heat treatment has been noted by the authors and fits in well, apparently, with a theory of the mechanism of heat treatment of these alloys that I have advanced in preceding papers.

I should also like to offer the suggestion that the structure, which Mr. Gibson has described, consists of grains of aluminum with a eutectic network of iron-aluminum compound, or iron-aluminum compound plus aluminum-copper compound. I think the suggestion of the authors was that this network might have been precipitated after solidification.

This structure is one with which all are familiar who have had anything to do with that of 88–10–2 bronze. In such bronzes large grains are obtained with a pronounced network within the grains; each grain consists of a dendritic crystal between the branches of which the eutectic has solidified later than the branches themselves. It would appear that the structure of the aluminum cast alloys is entirely similar in origin, and that the network is a real eutectic formed in a natural manner.

W. A. GIBSON.—In other words, you believe that the network is simply a discontinuous eutectic.

P. D. MERICA.—Yes, discontinuous network.

C. P. KARR,* Washington, D. C.—In work conducted by Doctor Merica and myself, we cast a number of these alloys at various temperatures, from about 670° up to 950°, and in one of his experiments some of the bars were poured at 950° and the heat held until the temperature dropped down to 650° and to 700°. The test bars cast at the higher temperature gave a very much lower result. At 700°, pouring from the same heat of metal, we obtained possibly the maximum physical properties of which the casting was capable. I would like to ask Mr. Gibson if he

* Associate Physicist, U. S. Bureau of Standards.

observed the pouring temperatures of the bars which he presented in his paper?

W. A. GIBSON.—The maximum furnace temperature was kept at 1400° F., plus or minus about 15°, and the pouring temperature was kept at 1300° in the ladle, that is, just before it was poured. The limits on this latter temperature would be plus or minus 5° or 10° variation.

H. S. RAWDON,* Washington, D. C.—It seems to me rather a nice way of looking at the structure is to think of each individual crystal as a pine tree. When these are jumbled together, you have just as many spaces between the branches as you have between the trees themselves; so there is really no more reason for the eutectic to collect at the boundary of the crystal than there is for it to collect in the spaces between the little branches of the trees. The micrographs do not suggest, strongly at least, that that second constituent comes out of the solid solution, rather it is the eutectic that forms from the molten residue after the formation of the trees, each tree being a tiny crystal in itself.

LEON MCCULLOCH.—I would suggest that these crystalline boundaries are not solid materials but voids formed by gases liberated during solidification.

P. D. MERICA.—As far as the alloys I have examined are concerned, the gas cavities, of which there may be a few present, are never present in that form, but in that of small rounded spots which are not usually numerous. Furthermore, the crystalline boundaries are not visible until after etching, as they should be if they are actual cavities.

W. A. GIBSON.—Of course the size of hole that can be seen undera microscope is limited only by the resolving power of the microscope and the polishing and etching of the sample. However, the cavities to which I referred as being penetrated by gas are smaller than can be seen by the ordinary microscope using, for example, 1000 diameters. There are usually a few holes visible in any section of aluminum. In inferior castings these holes may even be visible to the naked eye, but gas will pass through openings which are much smaller than those ordinarily visible in an aluminum casting under the best microscope.

The gentleman may have been misled by the appearance of Fig. 9. The black spots shown in this micrograph are not holes, but $CuAl_2$. It is to be noted that, in the type of etching given, the copper compound is black instead of light gray as in the sodium hydroxide etching given by Doctor Merica.

P. D. MERICA.—Will small castings of complicated design actually stand quenching in water without warping or cracking?

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* Associate Physicist, U. S. Bureau of Standards.

W. A. GIBSON.—Some cooling stresses would be set up, but nothing at all comparable to what you get in steel; I would not anticipate any difficulty in that direction. Our experience has shown that cooling in water or in oil will give better results than cooling in air, but we did not carry our experiments on air cooling very far because they did not seem to give much promise.

Influence of Heat Treatment on Gun Metal

BY C. F. SMART,* B. CH. E., ANN ARBOR, MICH.

(Philadelphia Meeting, September, 1919)

THE heat treatment of the bronze composed of 88 per cent. copper, 10 per cent. tin, and 2 per cent. zinc, has been investigated by H. S. and J. G. S. Primrose,[1] and also by the U. S. Bureau of Standards.[2] The results obtained by H. S. and J. G. S. Primrose on dry-sand castings subjected to reheating followed by air cooling, or by quenching in water, are shown in Figs. 1 and 2. The values for tensile strength have been

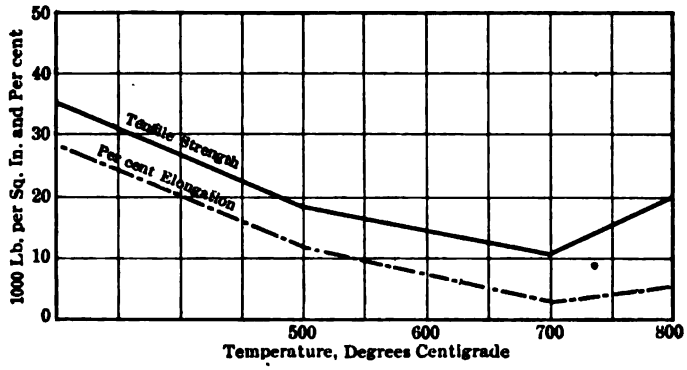

FIG. 1.—EFFECT OF QUENCHING ON DRY SAND CASTINGS (H. S. AND J. G. S. PRIMROSE).

converted from tons per square inch to pounds per square inch. Figs. 3 and 4, have been plotted from values obtained by the Bureau of Standards on material of the same composition and treatment. Both investigations show that the ductility of the cast bronze is improved by heating to 700° C. and cooling in air, the strength not being impaired by this treatment. They are not in agreement, however, as to the effect of quenching, Messrs. Primrose reporting a decrease, and the Bureau of Standards an increase, in both strength and ductility when the cast bronze is heated to 600° or 700° C. and quenched.

The present investigation was undertaken to study the effect of annealing followed by different rates of cooling, and, in particular, the

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* Assistant Professor of Chemical Engineering, University of Michigan.

[1] *Jnl.* Inst. Metals (1913) 9, 158.

[2] *Tech. Papers* 59 and 60.

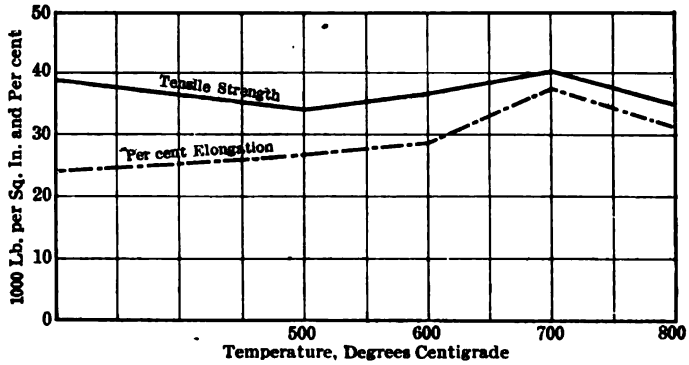

FIG. 2.—EFFECT OF ANNEALING ON DRY SAND CASTINGS (H. S. AND J. G. S. PRIMROSE).

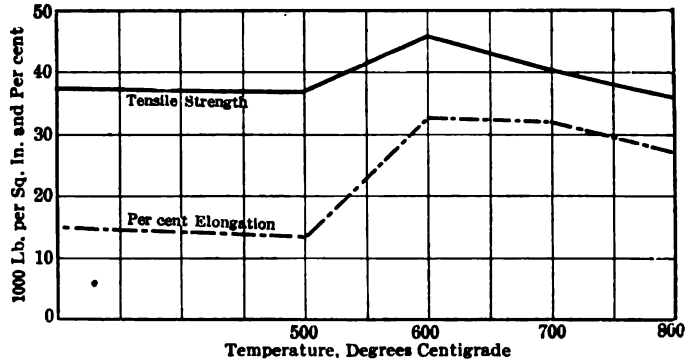

FIG. 3.—TESTS ON QUENCHED BARS (U. S. BUREAU OF STANDARDS).

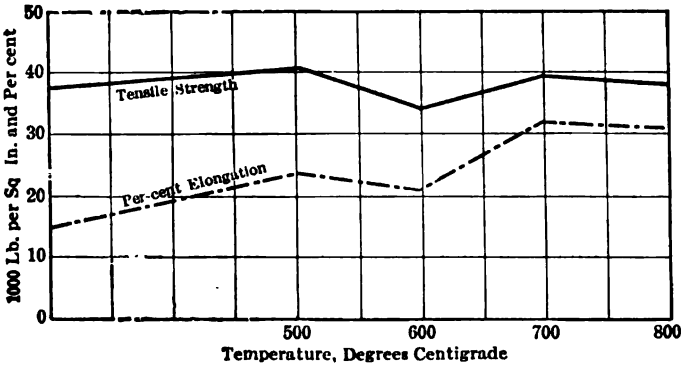

FIG. 4.—TESTS ON ANNEALED BARS (U. S. BUREAU OF STANDARDS).

effect of quenching. The test specimens used were sand-cast to size: 4 in. (101.6 mm.) long, 1 in. (25.4 mm.) diameter for a 0.75 in. (19 mm.)

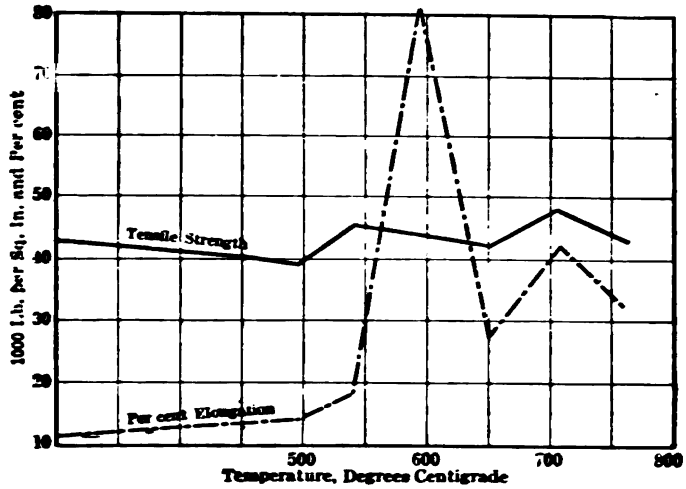

FIG. 5.—TESTS ON FURNACE-COOLED SPECIMENS.

length at each end, a 2 in. (50.8 mm.) gage length of 0.5 in. (12.7 mm.) diameter, and a 0.25 in. (6.35 mm.) curvature between the ends and

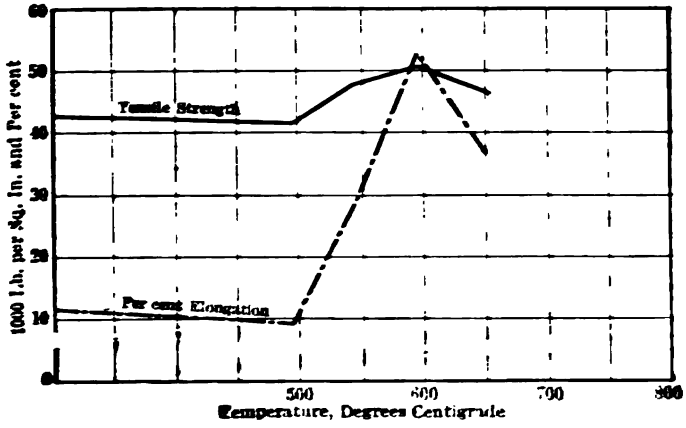

FIG. 6.—TESTS ON AIR-COOLED SPECIMENS.

middle portion. The bars represented a number of heats in commercial casting practice, analysis showing all heats to be within the composition limits: copper, 87 to 89 per cent.; tin, 9 to 11 per cent.; zinc, 1 to 3

per cent.; iron, less than 0.2 per cent.; and lead less than 0.2 per cent.; a standard specification for this bronze.

Heat treatment was carried out in an electric resistance furnace, the specimens being heated for a 30-min. period at the observed temperatures, 495°, 540°, 595°, 650°, 705°, and 760° C. From each temperature bars were

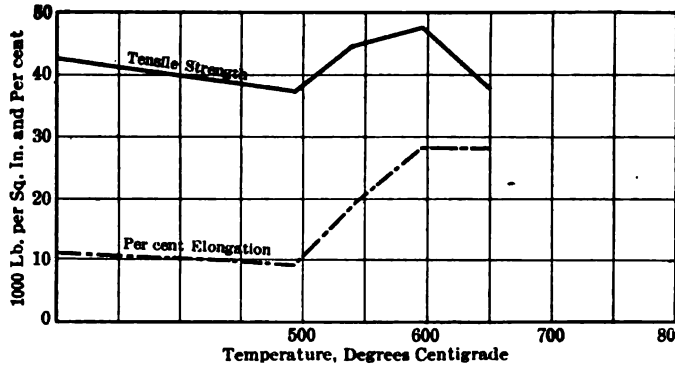

FIG. 7.—TESTS ON OIL-QUENCHED SPECIMENS.

quenched in water at room temperature and allowed to cool with the furnace, requiring about 24 hr. to cool from 700° to 75° C. From the first four temperatures of treatment, samples were also quenched in oil, and air cooled. These were broken in a tensile testing machine and the values for tensile strength and per cent. of elongation determined. The

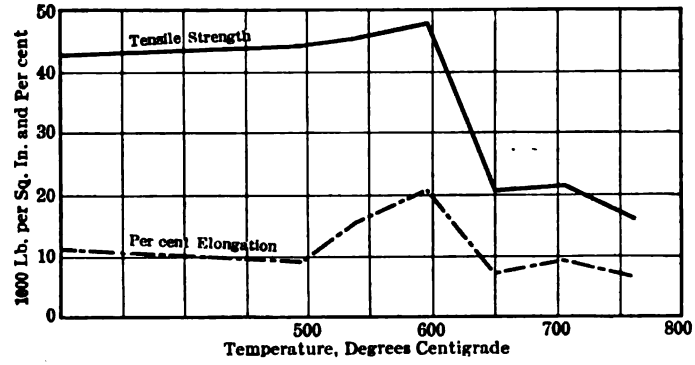

FIG. 8.—TESTS ON WATER-QUENCHED SPECIMENS.

results are given in Table 1, and plotted in Figs. 5, 6, 7 and 8. In every instance, the properties of the specimens heated to 595° C. are better than those of the cast material, and attention is called to the high elongation value of 81 per cent., with a tensile strength of 45,000 lb. per sq. in. (3163.5 kg. per sq. cm.) obtained on a specimen furnace cooled from this

temperature. The specimens quenched in water from 650°, 705°, and 760° C. were weaker and less ductile than the cast bars.

TABLE 1.—*Results of Tests*

Temperature, Degrees C.	Cooling	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent.	Temperature, Degrees C.	Cooling	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent.
Cast		43,100	12.5	595	Furnace	45,000	81.0
Cast		42,700	10.9	650	Water	23,650	10.9
495	Water	44,450	9.4	650	Water	18,400	4.7
495	Oil	37,125	9.4	650	Oil	38,000	28.0
495	Air	41,650	9.4	650	Air	50,500	48.5
495	Furnace	37,500	15.6	650	Air	42,900	25.0
495	Furnace	41,500	12.5	650	Furnace	42,350	28.0
540	Water	45,100	15.6	705	Water	24,600	11.0
540	Oil	44,600	18.8	705	Water	18,400	8.0
540	Air	48,000	26.5	705	Furnace	46,300	37.5
540	Furnace	45,550	18.8	705	Furnace	50,000	46.9
595	Water	48,100	20.0	760	Water	16,700	6.6
595	Water	47,650	21.9	760	Water	16,650	7.5
595	Oil	47,700	28.0	760	Furnace	42,200	32.9
595	Air	51,000	53.0	760	Furnace	44,300	32.9
595	Furnace	43,400	37.5*				

* Blowhole.

The fractures of the cast samples and of those heated at temperatures below 650° C. exhibited fine-grained material; those slowly cooled from the higher temperatures were also fine grained. The bars quenched in water from 650°, 705° and 760° C. were coarsely crystalline around the circumference and fine grained in the center, the coarse crystals extending radially to a depth of about 2.5 mm.

Microscopic examination showed that there was a gradual change in structure with increasing temperature of treatment, the dendritic structure of the cast metal becoming less distinct until at 760° C. it was no longer visible. In examining the structure of specimens quenched in water from 650° C. and higher temperatures, there were noticed a number of lines similar in appearance to fine cracks, extending from the edge toward the center of the pieces. Fig. 9 shows the appearance of these lines in the sample quenched from 760° C. They were not visible in the polished surface but were brought out by the etching treatment, using NH_4OH, and H_2O_2, and it appeared therefore that they were not cracks but were indications of strains produced by quenching and as such might be called incipient cracks.

To test this point, two test specimens were heated to 700° C. for 30 min. and quenched in water, brought back to the same temperature and

allowed to cool with the furnace. If the lines represented cracks in the metal the properties should be little affected by the reheating and slow cooling, if they were indications of strains, it should be possible to lessen their effect considerably by the second treatment. Physical tests gave the following values:

Bar	Tensile Strength, lb. per sq. in.	Elongation, Per Cent.
1	43,250	36.0
2	40,000	30.0

These values are somewhat lower than those obtained on samples slowly cooled from this temperature without previous quenching, but are much superior to values obtained by quenching only.

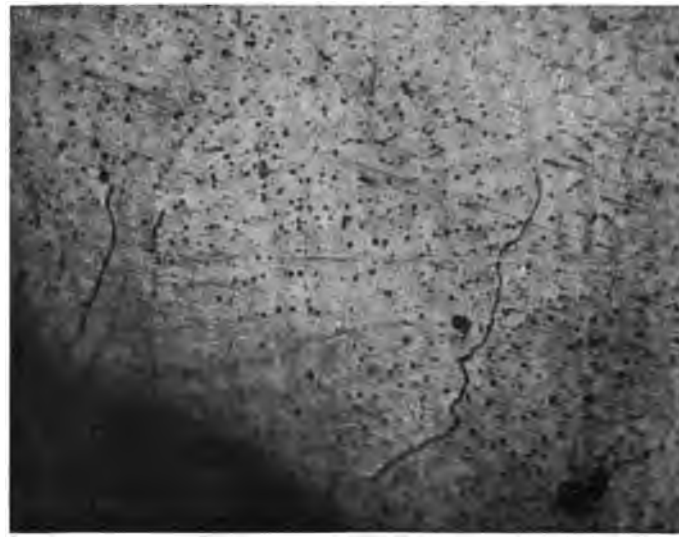

Fig. 9.—Specimen quenched in water from 760° C. × 75.

From a comparison of the results of physical tests, the appearance of the fractured bars and the microstructure, it became apparent that all the specimens that were lacking in strength and ductility, that is those quenched in water from 650°, 705°, or 760° C. had a partly coarse fracture and showed strain lines; all other bars had a fine-grained fracture and no strain lines in the etched surface. This indicated that the low values for strength and elongaton of these quenched samples were due to a condition of strain in the surface portion of the bars. To determine whether such was the case two specimens were water quenched from 700° C. and then machined down over the gage length, from 0.5 in. (12.7 mm.) diameter to 0.442 and 0.421 in. (11.2 and 10.7 mm.) diameter, respectively. Physical tests gave the following values:

Bar	Diameter, Inch	Tensile Strength, Lb. Per Sq. In.	Elongation, Per Cent.
1	0.442	44,000	21.8
2	0.421	35,500	15.6

The fracture of No. 1 was entirely fine grained, that of No. 2, still retained a narrow band of coarse crystals. The first sample behaved in testing like all ductile pieces, the elongation taking place throughout the gage length with the production of a crinkled surface. The second sample acted somewhat like the brittle pieces, cracking in several places along the gage length during the pulling operation.

Turner and Haughton[3] give curves on the contraction of solidified copper-tin alloys and state that from the curve of the alloy with 20 per cent. tin, it appears that there is a volume change at 500° C. They also mention a difference in the coefficient of expansion and contraction of the alpha and beta solid solutions of the copper-tin series. Messrs. Primrose refer to a similar difference and add that when the beta solution breaks up into the eutectoid, microscopic crevices occur between the delta and secondary alpha constituents. Specific-gravity determinations also point to some such change. Three bars heated to 620° C. and slowly cooled showed an average decrease in specific gravity of 0.059. Two samples cut from the same casting, given the above treatment but polished before each determination, gave an average decrease in specific gravity value of 0.039. These tests are very brief but they indicate an expansion on heating and slow cooling the cast metal, and considering the possibility of microscopic crevices between two constituents of the casting, the change in density would not necessarily be a true measure of the total expansion.

Consideration of the results given leads to the conclusion that this bronze is subject to quenching strains that may affect values for strength and ductility obtained from quenched test bars. Bars in which a condition of strain existed gave comparatively low values for these properties, while if the strained part was machined away, much higher values were obtained. It is probable that the difference in results of the previous investigations arose from this fact. The heat-treatment work of the Bureau of Standards was based on bars cast $\frac{9}{16}$ in. (14.2 mm.) in diameter; and although it is not definitely so stated, it is presumed that the bars were treated and then machined for testing. Messrs. Primrose state definitely that their test specimens were machined to finish size for testing, before heat treating, so that the properties of the quenched bars, would have been influenced by a part of the metal being in a strained condition.

[3] *Jnl.* Inst. Metals (1911) 6, 192.

DISCUSSION

R. F. Wood,* Sandusky, Ohio.—I made a few tests of gun-metal specimens, after I noticed the results on quenching reported by the Bureau of Standards. The data of one such test are given herewith. The bars were heat treated and quenched before they were machined, and in all cases they were brought up to 700° or 800°. They became extremely brittle, showed almost no elongation, except such as was caused by the failure of the pieces to fit together after they were pulled,

Group	Heat Treatment	Bar	Ultimate Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.
B	No heat treatment whatever	1a	35,900	21,150	15.0
		2a	36,400	23,000	17.0
C	To 800° (10 min.*); cooled slowly in furnace (over 7 hr.)	3a	37,750	23,250	28.5
		4a	35,800	20,300	25.0
D	To 800° (20 min.); cooled in air (35 min.)	1b	36,200	22,850	21.5†
		5a	36,100	22,000	22.5†
E	To 800° (25 min.); cooled to nearly black in furnace (25 min.); then in air (30 min.)	4b	30,900	21,450	17.5
		6a	38,500	22,050	26.0†
F	To 800° (25 min.); cooled to nearly black in furnace (25 min.); then quenched in water.	2b	(Broke to pieces in lathe)		
		5b	7,500		2.5
G	To 800° (20 min.); quenched in water immediately.	3b	13,100		1.0†
		6b	14,500		4.0

* Time given in parentheses refers to time required for operation mentioned.
† Broke outside of gage length.

and the tensile stength was reduced from around 35,000 to about 13,000 lb. per sq. in. In addition, the weakening effect of the quenching seemed to be almost as marked when the bar was allowed to slowly air-cool from red to black, and then quenched, as it was by quenching directly from the red heat.

* Metallurgist, Sandusky Foundry & Machine Co.

Test Bars.—Rough size, 9/16 in. diam. over test section, grips 13/16 in. diam. Cast two in a flask, one on each side of a block 8 by 4 by 1 in. and fin-gated thereto from the grips but not from the test section. Poured with flask in inclined position, with gate to lower end of block and riser from upper end of each test bar. Bars were machined to ½ in. over the test section, after heat treatment.

Casting the Bars.—Charge of 1500 lb. consisting of 400 lb. of new metals and 1100 lb. of G turnings and scrap was melted in open-flame oil furnaces and then poured into a 1-ton ladle. From the ladle 150 lb. was poured into a preheated No. 50 crucible, and from this the flasks of test bars were poured. The six flasks are indicated by the numbers 1 to 6 and the bars in each flask by the letters a and b, thus 4a and 4b, for instance, were the two bars in flask No. 4.

Heating the Bars.—In all cases the bars were introduced into an already hot electric muffle and brought up to a temperature of about 800°, less rather than more, as gaged by a Leeds & Northrup optical pyrometer. The cooling was then commenced at once without the bars remaining at the attained heat. Two pairs of bars were heated at a time; groups D and G were heated together in the furnace, groups E and F together, and group C by itself. It will be observed that the pairing off by flask numbers and group numbers was so arranged as to reduce the chance of wrong deductions, such as might arise from abnormal conditions in any one flask of bars or in any one muffle load during heat treatment.

P. E. McKINNEY,* Washington, D. C.—The question of heat treating red bronzes is of great importance to the foundryman who is producing any quantity of red bronze castings. The data and the information we have on heat treating and on annealing are only elementary. The effects of slow cooling from the molten state, in the case of heavy cross-sections can practically be eliminated and remarkable increases in strength and ductility obtained by the annealing or the heat-treating process. The strain cracks referred to probably have been encountered by others, but castings containing them have generally been ruined before an attempt to heat treat them is made. In other words, the pouring temperature was too high, or the strains due to the large segregations of enriched eutectic caused intercrystalline cracks or parting in the metal. Conditions like that cannot be corrected by heat treating any more than a steel forging or a steel casting can be welded by heat treating. If the crack or the opening is there, it remains there.

It has been quite noticeable, in our experiments in heat treating red-

* Chemist and Metallurgist, U. S. Naval Gun Factory.

bronze castings, that the quench is really necessary to get the very best results in the case of a heavy cross-section, for the reason that the alpha constituent in a heavy section, slowly cooled, grows to very large grain size. The quench corrects this and, if followed by an anneal at a lower temperature, draws the strain out of the casting, frees the casting of enlarged grains of the alpha constituent, and the eutectic, in which the constituent has frozen out, is again divided into very fine grains and uniform structure with considerable increase in strength and ductility.

W. M. CORSE, Mansfield, Ohio.—Mr. McKinney, in quenching castings such as you have just mentioned, is there danger from actually cracking those castings during the quenching operation?

P. E. MCKINNEY.—There is considerable danger, especially if the castings are large; not so much from the effect of the quenching medium as from the handling of heavy sections. At approximately red heat, red bronze is one of the most tender metals. A piece of 88–10–2 bronze hit, when hot, a slight blow with a baseball bat will fly to pieces; that is, it will crumble. These castings must be handled very carefully. Some castings, in the shape of tubes, weighing about 3000 lb. could be handled only by putting them into a pit, suspended on a crane, and then picking them up and throwing a spray of water around them. It did not seem that the dipping in the water or the effect of the water was as bad as the sudden strain of picking them out of the furnace with a peel and handling them when immersing into the quenching medium. Oil seems to give no different results than water; so it is hardly a case of the effect of cracking due to sudden change of temperature.

W. M. CORSE.—There seems to be hot shortness in the casting itself.

P. E. MCKINNEY.—Yes; the casting will not stand the strain of its own weight if handled at those high temperatures. We would not think of removing a casting from the sand at the temperature that you would pick it up and quench it.

W. M. CORSE.—Do you believe it is possible to handle the casting so that the desired results may be obtained?

P. E. MCKINNEY.—Only by the same methods that you would use iu handling forgings and big pieces of steel in quenching. We heat the casting in a vertical furnace so that the crane picks it up and, practically without any jarring, carries it to the quenching pit.

GEO. F. COMSTOCK,* Niagara Falls, N. Y. (written discussion).—This interesting paper throws additional light on a question about which

* Metallurgical Engineer, The Titanium Alloy Mfg. Co.

differences of opinion have apparently existed in the past, and the writer would like to record in this connection the agreement of his experience with that of Primrose and Prof. Smart in regard to the effect of quenching on the properties of gun-metal bronze. The writer's results have been published,[4] so that there is no need for a detailed report here, but his investigations resulted in showing that both gun metal and manganese bronze are ruined by quenching in water from a red heat, apparently because they cannot stand the strains produced by the sudden cooling.

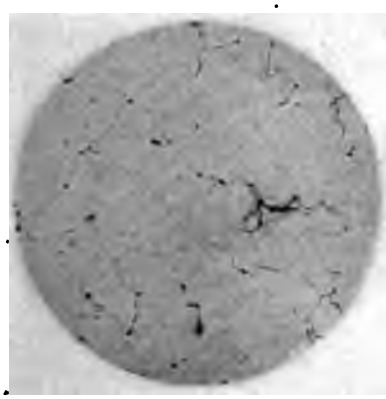

FIG. 10.

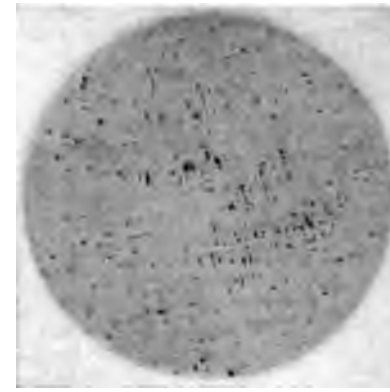

FIG. 11.

The lines, mentioned by Prof. Smart, in a polished and etched section of the quenched metal have also been noticed by the writer, who however has not found them any different in quenched specimens than in annealed specimens. Since they appear only after etching, it would seem most probable that they are merely grain boundaries in most cases, though Prof. Smart's idea that they are indications of strains is by no means impossible. Fig. 10 shows how these lines appeared on the author's specimens of annealed gun metal, etched with ammonia and hydrogen peroxide, and magnified 100 diameters.

Prof. Smart's specific-gravity determinations are interesting in connection with the writer's experience that the annealed bars are always much more porous than the same alloy was when cast. Fig. 11 shows an especially porous specimen of this alloy, etched like Fig. 10 and magnified 20 diameters, which however seemed sound when tested and gave over 45,000 lb. per sq. in. tensile strength and 40 per cent. elongation. The writer's idea of this porosity was that in the cast metal there were inclusions of gas in the form of films between the dendritic crystals, and that these films were so thin that they escaped detection under the microscope.

[4] *Foundry* (Apr. 15, 1919) **47**, 189.

Upon annealing, the films were thought to contract by surface tension, and the gas then formed rounded cavities which were much more noticeable on the polished surface. From the lower specific gravity which Prof. Smart has shown, it seems as though the included gas had actually expanded the metal somewhat in forming these more rounded cavities.

The range of composition that Prof. Smart allowed in his test bars, namely from 9 to 11 per cent. tin, was far too large for obtaining check results, as very different results would be obtained with these two tin contents even with identically the same treatment. Doubtless some of the irregularities in his curves are due to variations in analysis. The paper is of great interest and helps to clear up an uncertainty that existed in connection with the results of quenching this well-known alloy.

Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod*

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(Philadelphia Meeting, September, 1919)

THIS paper was prepared upon request as a contribution to a symposium covering the manufacture, properties, and uses of the important non-ferrous metals.

In approaching a subject as broad as this, there is a natural desire to build up a comprehensive and finished production which shall constitute a dependable source of information on all questions properly belonging to this branch of metal technology. There are, however, a number of circumstances, apart from the mere routine of labor and thought involved. which operate rather effectively against the possibility of completing such an ambitious program at the present time.

First of all, as far as any public record of results is concerned, the commercial rolling, drawing, and forming of zinc with relation to changes of structure and properties—and this we consider to constitute the elements of metal technology—might as well be an unpractised art. We have never seen a published photomicrograph showing the structural characteristics of either hard or soft sheet or strip, although the structure of castings has been frequently described, and other coarse-grained structures resulting from hard-hammering and annealing have been reproduced. Thus, an author in this field must proceed to his task without much assistance from the literature, and the outcome can represent only a personal estimate of principles, facts, or findings, and not a summary or survey of progress in the entire field as determined by varied experience, practice, and settled opinion.

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Again, zinc is becoming prominent as a substitute for copper, brass, or aluminum in spinning, stamping, cupping, drawing etc., but the details of practice which have been developed in different mills for rolling the sheet or strip have not become the common property of all, and the constant effort to produce metal of superior qualities or finish is naturally an effort of individual initiative. The information which we are able to present has been developed mainly at the plants and in the laboratories of the New Jersey Zinc Co. and has been selected with a view to its general bearing on zinc metal problems rather than on any specific or local mill problems. We would, in fact, regard it as highly inappropriate to seek authorization to publish actual mill schedules or to assume responsibility for contributing details of the rolling practice at the Palmerton Mill.

Finally, much of the information which would be required to fully establish the comparative merits of zinc and other ductile metals or alloys in the face of widely varying manufacturing or service requirements is virtually non-existent. We do not feel qualified to write authoritatively or at length on this aspect of the subject, viz., on what might be termed "comparative metal technology." Data of this sort will gradually accumulate, and until sufficient evidence is at hand, many of our opinions as to the adaptability of zinc in competition with other metal already established in a given service must be in part speculative and in part based on such elementary properties as have been adequately described.

The foregoing introductory remarks will perhaps serve to explain what may appear to be a rather inadequate presentation under an asuming title. We hope that this paper may at least set forth some of the more essential scientific aspects of the subject in hand and that it may be followed by others carrying the subject still further.

In this paper the following topics will be discussed in the order indicated.

1. Rolled zinc as described in the existing literature.
2. The properties and behavior of zinc from a theoretical point of view.
3. The effect of the ordinary rolling variables on zinc as compared with copper and the copper base alloys: Factors controlling the "temper" of rolled zinc.
4. Static properties of soft, medium and hard strip zinc before and after annealing.
5. Dynamic ductilities.
6. Stiffness of worked zinc; alloyed products.
7. Successful applications.

1. Rolled or Worked Zinc as Described in the Existing Literature

There are about a half-dozen published papers which may be profitably read by those interested in the general nature and properties of worked zinc. These papers constitute the nucleus of the technical literature in this field and while they collectively offer a certain survey of the mechanical properties of ordinary rolled or drawn zinc, they fail to give any adequate characterization of the true physical condition or structure of the metal tested. Naturally, they leave us without information as to the ordinary range or variation of properties which may be expected in this type of material as a result of specified treatment.

The first three of these publications are of German origin, viz., (1) J. Bauschinger. Einfluss der Zeit bei Zerreissversuchen mit verschiedenen Metallen. Mitteilungen aus dem mech-technischen Lab. der Technische Hochschule in München. Heft 20 (1887). (2) A. Martens. Festigkeitsuntersuchungen mit Zinkblechen der Schlesischen Aktien Gesellschaft für Bergbau und Zinkhüttenbetrieb zu Lipine 0 = *S.* Mitteilungen aus dem Königlichen technischen Versuchsanstalten zu Berlin. Ergänzungsheft IV (1889). (3) O. Meyer. Uber die Eigenschaften von Zinkblech und dessen bleibende Zustandsänderungen bei verschiedenen Legierungen. Oesterreichische Zeitschr. für Berg und Hüttenwesen, Oct. (1905).

All three authors give tension tests on rolled metal, and summaries of certain of the principal data, recalculated into English units, have been included by (4) H. F. Moore in a more modern paper entitled "An Investigation of the Strength of Rolled Zinc." Univ. of Illinois *Bulletin*, vol. 9, No. 9 (1911).

The following comments will define the class of data and some of the uncertainties associated with these papers: Bauschinger tested pieces cut parallel to the direction of rolling from a sheet of Upper Silesian rolled zinc 0.07 cm. thick (about 0.028 in.). No further characterization of the metal was given. The milled test section was 3 cm. wide and 15 cm. long. He pulled the strips at four different speeds, viz., the several tests were completed in 6¼, 22½, 37½, and 81 min., respectively. A table of results includes maximum load, breaking load, contraction, and elongation (15 cm.).

In the 6-min. test the break occurred so soon after the maximum load had been reached that the breaking load could not be read. In other cases the breaking load was about 80–90 per cent. of the maximum load. Both maximum load and breaking load increased with the rate of loading. The highest and lowest maximum load strengths were about 30,100 and 24,100 lb. per sq. in.

The contraction of area remained substantially constant, while in the

words of the author "the elongation (10 to 20 per cent. in 15 cm.) seemed to depend more upon incidental unknown circumstances than upon the speed of testing." It may be well to add that the author found no relation between the rate of loading and the strength of cast zinc. His samples gave an average maximum load strength of about 3500 lb. per sq. in.

Martens' paper is a much more extensive one and it contains a very minute description of his experience in tension tests with zinc. We quote him substantially as follows in his introductory description of the characteristics of rolled zinc in tension:

"In the tests it became evident at once that one cannot make use of loading by direct application of weights with any prospect of success if one desires a correct picture of the behavior of the material. Zinc is in a very high degree influenced by the rate of performing the test. The maximum load is reached immediately after the material begins to stretch noticeably, and practically the whole extension up to the break occurs after the maximum load has been reached. The force necessary for flow of the body under definite constant rate decreases steadily and it is impossible, in view of the great sensitiveness of zinc in this respect, to change the weights evenly enough to avoid clouding the results."

In order to overcome the difficulties with his first machine, the author after much experimentation constructed a machine which operated at a chosen constant speed and autographically gave the changing load through a hydraulic measuring device. This machine was evidently very sensitive and the results reported deserve careful attention. The actual behavior of zinc in the tensile test was described in detail. A number of tests were made in which the machine was suddenly stopped while the specimen was stretching. During the pause of 1 min., the load previously obtained decreased spontaneously, accompanied by further stretch of the specimen, until a lower equilibrium value obtained. For 1-min. pauses, the load dropped in some cases to about half its former value. (Average of 63 per cent. in 73 tests.)

After preliminary tests with earlier machines, Martens made tests on plate rolled in one direction from a slab 300 mm. wide to three times its original length, using his latest machine of 50,000 kg. capacity with autographic mirror attachment to indicate a graphical relationship between load and deformation. The final thickness of the material was 5.4 mm. (0,213 in.). Analysis of the metal showed: lead, 1.06 per cent. and iron, 0.02 per cent. No other elements were determined.

One of Martens' tables, according to which the increase in stress occurred in stages, most of them followed by a stage in which the stress was lowered to 185 lb. per sq. in., is given below. The area of the test section was 4.4 by 9.0 mm. The speed of operating the machine is not given.

TABLE 1.—*Stress-strain Data from Rolled Zinc Plate. (Martens)*

Stress, Lb. per Sq. In.	Total Elongation Under Load—Ten Thousandths of 1 Mm.	Permanent Set—Ten Thousandths of 1 Mm.	Stress, Lb. per Sq. In.	Total Elongation Under Load—Ten Thousandths of 1 Mm.	Permanent Set—Ten Thousandths of 1 Mm.
185	0		1792	260	
356	20		185		64
185		2	2688	437	
711	63		3584	634	
185		1	185		178
1081	106		3584	673	
185		4	185		229
1437	156		3584	777	
185		11	185		283
1437	161		3584	763	
185		16	185		292
1437	164		3584	767	
185		18	185		304
1437	171		4495	976	
185		19	5391	1380	
1437	172		185		567
185		20	5391	1430	
1792	237		185		647
185		37	5391	1495	
1792	255		185		685
185		57	5391	1545	
1792	252		185		750
185		57	5391	1589	
1792	259		185		782
185		61	6287	2062	
			7155	2660 metal flowing slowly	

On the basis of this and similar tests the author writes that there can be no consideration of a true elastic behavior in rolled zinc plate; the permanent set increases after each stage of loading even in the case of very small loads. In fact, where the change from higher to lower load is repeated, the respective changes (drops) in elongation appear to vary among themselves.

Other tests with this material gave clear indications that with stresses under some 2000 lb. per sq. in. the specimen continues to stretch from minute to minute as the load is maintained. Further tests on the influence of the time factor are given in Table 2. These tests presumably correspond to (relatively high) stresses at which the metal had begun to stretch noticeably

TABLE 2.—*Effect of Interruption During the Tensile Test of Zinc Plate (Martens)*

Test No.	Percentage Decrease of Load at Expiration of:						
	10 Min.	6 Min.	5 Min.	4 Min.	3 Min.	2 Min.	1 Min.
1	73.7	66.0	65.3	61.0	61.7	53.9	44.0
2	88.2	78.9	74.1	74.6	62.4	51.9	42.4
3	72.4	61.9	60.9	59.3	59.0	44.8	34.8
Average.....	78.1	68.9	66.8	65.0	61.0	50.2	40.4

Similar indications may be obtained more conveniently by varying the speed of the testing machine, *i.e.*, operating first at a given speed and then suddenly raising or lowering the speed to a different value. According to this procedure, stress-deformation curves of the type shown in Fig. 1 will result.

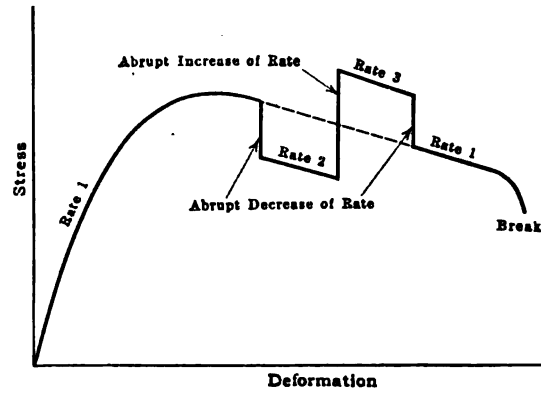

FIG. 1.—EFFECT OF CHANGE OF RATE OF LOADING IN THE TENSION TEST WITH ZINC (*Martens.*)

After describing the principal characteristics or peculiarities of rolled zinc in the tension test, Martens reports data from three main groups of experiments, viz.,

1. Tests at room temperature with material taken from the mill stock of the "Schlesische Aktiengesellschaft für Bergbau und Zinkhütten betrieb zu Lipine in Oberschlesien," and with competitive material.

2. Tests at the several temperatures; 80°, 120°, 150°, 170° and 200° C., with plate 0.6 mm. thick also taken from stock.

3. Tests at room temperature with a series of eleven plates or sheets, each representing a stage in the course of rolling from an initial thickness of 5.6 mm. (end of stage 1) to a final thickness of 0.48 mm.

The first three stages represent rolling in one direction to two, three, and four times the original length, respectively; while the last eight stages

represent pack-rolling to decreasing thickness in a uniform direction after previous rolling from an initial length of 300 mm. to one of 710 mm. in the other major direction. During pack-rolling, a sample was taken after every 500 mm. increase in length.

The several different materials tested all showed about the same lead and iron contents by analysis, viz., close to 1 per cent. and 0.02 per cent. respectively.

The test pieces were cut from the plate or sheet to represent both major directions. They were milled to give a narrowed central section of the usual type. Full dimensions are not given. Most of them were pulled at a rate of 0.77 mm. (0.03 in.) per minute.

These tables give data of the following character: Thickness, area of test section, maximum load (taken from the autographic record), percentage elongation in 100 mm. (measured in the usual manner after fracture), area of the stress-deformation diagram. "Völligkeitsgrad" = ratio of area of diagram to area of limiting rectangle (maximum load × maximum deformation under load). "Arbeits vermögen" = maximum load $\times \frac{\text{per cent. elongation}}{100} \times$ "Volligkeitsgrad" $\times \frac{1}{\text{sp. weight, or } 7.20}$.

A reasonable number of tests (five or six) were made in order to get a reliable average in each case and the author makes special mention of the disturbing irregularities encountered in testing rolled zinc; viz., "external influence such as local failure and action of the grips are of considerable effect, so that it is absolutely necessary to take the average from a large number of tests."

In the first series of tests, five "Silesia" sheets (thickness 0.22 to 1.06 mm.) show in the direction of rolling average tensile strengths from 19,487 to 28,163 lb. per sq. in. and average elongations from 12.2 to 22 per cent. in 100 mm. At right angles to the direction of rolling, they show tensile strengths from 21,762 to 30,154 lb. per sq. in.; and percentage elongations from 8.2 to 13.5.

Two sheets of competitive material (0.66 and 1.03 mm. thick) show in the direction of rolling average tensile strengths of 18,064 and 17,495 lb. per sq. in. respectively; and percentage elongations of 11.2 and 14.4. In the other direction, corresponding figures are 19,202 and 27,879 for tensile strength and 14.2 and 17.8 for elongation.

There is hardly any use in discussing the comparative data from tl above tests as the details of manufacture of the sheet used are obscure.

The fact that the "Silesia" sheet is weaker and more ductile in the direction of rolling than in the crosswise direction, while the competitive sheet is weaker and less ductile in the direction of rolling than in the crosswise direction, can only be explained with relation to the quantity and direction of fiber brought about in the rolling operations. Doubtless, the competitive sheet before final rolling had been reduced extensively in a crosswise direction.

In view of the interest attached to the strength and ductility of zinc at elevated temperatures, we reproduce here Martens' table of tests dealing with this subject (values designated as "Völligkeitsgrad" and "Arbeits vermögen" are not included). It should be noted, however, that the character of the sheet used is not well established. It is merely designated as sheet about 0.6 mm. thick, taken from stock, and containing 1 per cent. of lead and 0.02 per cent. of iron.

TABLE 3.—*Martens' Tests of Strength and Ductility of Rolled Zinc at Elevated Temperatures*

Temperature, Degrees C.	Ultimate Tensile Strength Lb. per Sq. In.		Percentage Elongation in 100 (?) mm.	
	Direction of Final Rolling	Crosswise Direction	Direction of Rolling	Crosswise Direction
Room	19,487	21,762	12.2	12.6
80	12,232	12,659	27.8	31.0
120	7,965	9,957	66.7	52.1
150	5,263	6,116	112.7	90.2
175	7,965	7,823	22.1	12.1
200	5,832	6,258	9.0	5.4

Martens' principal conclusion from these results is that it would appear advantageous to conduct all operations on zinc which bring about a pronounced change of form, *i.e.*, rolling, pressing, stamping, etc., with heated material in so far as the operation itself does not supply the heat; since at 150° C. there occurs a combination of low strength and high ductility. Some comment of this subject will be given later.

The third and last group of tests by Martens is fairly extensive and the metal used is rather better characterized than was the case with previous tests. These tests give the strength and ductility of plate or sheet passed from one stage to another in the rolls, and the direction of rolling and thickness from stage to stage are clearly indicated, as already noted.

These tests, in general, show an increase both of strength and ductility as the rolling progresses, marked by very considerable irregularities in the thinner gages. The author was unable to explain these variations in the absence of knowledge as to the structural characteristics of the material at different stages.

Since we shall be able to show a similar series of tests in which structure and properties are correlated (Section 3) there is little to be gained by further discussion of Marten's tests.

Meyer tested a greater variety of material as regards its chemical composition but he dismisses all questions as to preparation of the sheet with the brief statement that it was rolled in the "staatliche Zinkhütte Cillis in Südsteiermark."

The following nine varieties were used:

	Lead, Per Cent.	Cadmium, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Arsenic
1	1.04	0.05	0.020	0.009	Trace
2	0.024	0.047	0.026	Trace	Trace
3	0.100	0.244	0.023	0.00096	Trace
4	0.021	0.402	0.021	Trace	Trace
5	Same as No. 4 but unevenly alloyed.				
6	0.025	0.59	0.023	Trace	Trace
7	0.025	0.912	0.024	Trace	Trace
8	0.81	0.732	0.03	Trace	Trace
9	0.81	0.03	0.03	Trace	Trace

Meyer's principal tests were made on material (1) as received (2) after 1 min. treatment with 5 per cent. nitric acid or (3) after annealing for a period of 1 hr. at 275 ± 5° C. The thickness of the sheet was in the neighborhood of 2 mm., while the length of the test section was 15 cm. and the width approximately 2 cm.

Much attention was paid to the elastic properties of the material and while values for modulus of elasticity, elastic limit, and limit of proportionality are reported, the author freely concedes their indefinite character and we doubt if they have any real value. It is, however, claimed that the annealed samples, as contrasted with the samples in their original condition, exhibited a definite elastic behavior, although at very low stresses. For example, values up to 3500 lb. per sq. in. are reported for the elastic limit of annealed material and up to 2500 lb. per sq. in. for the limit of proportionality.[1] No particular relationship between these values and the chemical composition can be discerned.

Although it is not clear just what annealing procedure, in addition to that given above, was undertaken by the author, he gives in a general summary of results the various temperatures at which the different kinds of material first anneal, or undergo a "transformation"—principally in the sense of deterioration.

These "transformation temperatures" are as follows:

Material No.....	1	2	3	4	5	6	7	8	9
Transformation temperature, degrees C.....	155	155	165	145	145	145	145	145	145

[1] The highest stress which produces no detectible deformation is greater than the highest stress at which stress and deformation retain their proportionality. Both values of stress are very low, that is, the material fails almost from the beginning to follow Hookes's law, as the deformation commences to accelerate at once. This acceleration naturally increases as the stress rises to relatively high values. There is a fairly linear portion of the stress strain curve along which an approximate (variable) modulus of elasticity can be calculated.

It makes little difference how long the material is annealed at the transformation temperature; the characteristic change in properties is produced even after an anneal of 1 minute.

It appears unprofitable to discuss the effect of annealing at this time, as considerable data of a more definite character will be presented in this paper, and certain factors which profoundly influence the annealing characteristics of rolled zinc can be specified in due course.

Meyer's tests after acid treatment were undertaken to determine the effect of an etching treatment approximating that frequently applied commercially (to lithographers plates, etc.) on the mechanical properties of the metal. He found that such treatment had little or no effect. The metal was not embrittled and it retained its normal tensile characteristics, quite contrary to what has been experienced in the case of other metals, notably iron, probably owing to gas absorption.

We give here a table summarizing some of the more important tests published by Meyer, with the comment that the elastic properties, and "Quality Coefficients" reported by him are not included, as it does not seem advisable to introduce a lengthy discussion of these tests.

Obviously, the effect of annealing all of the above material has been to impair both strength and ductility. It will be pointed out later that results of an entirely different character may be obtained with certain varieties of rolled zinc.

On the basis of his annealing experience, Meyer argues at large concerning the effect of temperature in the rolling or working of zinc. He affirms positively that rolling at a temperature much higher than 150° C. would yield an inferior product whose properties would correspond with those of "transformed" or annealed zinc. Furthermore, he finds support in Martens' tests at elevated temperatures for a contention that the allowable temperature limits for successful rolling or working of zinc are quite narrow—not far removed in either direction from 150° C.

Such conclusions are altogether too broad and founded on insufficient evidence. The rolling temperature may be properly varied between wide limits depending upon the kind of metal to be rolled and the properties desired. Rolling at or above the so-called transformation temperature need not produce a "transformed" (*i.e.*, coarsely crystallized) zinc. There is considerable difference in the grain characteristics produced by annealing a cold-worked or strain-hardened product and by direct working at the effective annealing temperature. This is a commonplace observation taken from general metallographic experience and it merely serves to emphasize the necessity of considering the whole group of rolling variables before specifying the effect of any one of them.

Moore's tests were made with eighteen sheets of rolled zinc, each 18 by 20 in., furnished by the Matthiessen & Hegeler Zinc Co. and varying

TABLE 4.—*Summary of Tension Tests.* (*Meyer*)

		Kind of Material	1	2	3	4	5	6	7	8	9
Average of results in the direction of and at right angles to the direction of rolling	As Received	Ultimate tensile strength, lb. per sq. in.	36,555	33,141	29,159	35,986	35,133	33,426	32,146	33,568	32,288
		Percentage elongation	17.2	16.2	38.3	18.0	16.0	24.6	12.0	3.6	20.2
		Contraction of area	27.0	30.0	56.0	35.0	23.0	37.0	29.0	6.0	25.0
		Number of cold bends (back and forth)*	6.0	12.0	17.0	6.0	9.0	7.0	6.0	2.0	9.0
	After Anneal	Ultimate tensile strength, lb. per sq. in.	.....	14,082	20,340	17,353	.....	5,405	20,909	15,219	15,219
		Percentage elongation	.....	5.7	9.0	3.5	.....	3.5	2.4	1.5	6.8
		Contraction of area	.....	6.0	9.0	5.0	.....	4.0	2.0	2.0	9.0
		Number of cold bends (back and forth)*	.....	2.0	4.0	2.0	2.0	1.0	1.0	2.0	3.0

* Details of procedure not given.

in thickness from 0.006 to 1.0 in.; with samples of sheet zinc purchased in the local market; and with a few specimens of cast zinc.

No analyses are given and likewise no details as to the manufacture of the sheet.

The cast zinc was tested in tension, in compression, and in torsion.

The rolled zinc was tested in tension, in cold bending, and in shear (punching tests and tests in direct shearing). Quite a number of stress-deformation diagrams are given and comparisons with steel plate are shown.

Moore's experience in studying the elastic behavior of this material was similar to that of the earlier authors. "A set was detected in most tests after the removal of the first load applied, however low."

A stress-compression diagram from cast zinc and a stress-deformation diagram from rolled zinc, both made to represent steadily increasing repetitive loading, indicate a pronounced loss of energy, or mechanical hysteresis, during the release and re-application of the load. This condition was clearly foreseen by Martens.

In view of the fact that Moore's paper is more readily accessible than the papers previously reviewed, we will forego any reproduction of his tables.

His own summary is, however, quoted as follows:

1. Zinc either rolled or cast has no well-defined yield point and its elastic limit is very low. Zinc possesses a relatively high degree of plasticity.

2. The ultimate tensile strength of thin rolled zinc plate (not more than 0.05 in. thick) is about 24,000 lb. per sq. in.

3. The modulus of elasticity of zinc in tension is about 11,500,000 lb. per sq. in.

4. The stress per square inch of area sheared developed in punching or shearing rolled zinc plates is about 40 per cent. of the stress developed in punching or shearing mild steel plates.

5. The energy per square inch of area sheared per inch thickness of plate required to punch or shear rolled zinc plates is about 30 per cent. of the energy required to punch or shear mild steel plates.

6. The ductility of rolled zinc is much less than that of mild steel,[2] and the ductility of zinc plate with the grain is greater than the ductility across the grain.

The fourth paper to be considered—(4) M. G. Timofeeff. Sur la Récristallisation du Zinc Écroui. *Revue de Métallurgie*, vol. 11 (1914), pp. 127–132—is of an entirely different character from the others, in that it contains no record of mechanical properties but is devoted to the microscopic metallography of zinc. It is the first paper in this field.

[2] The reader should not accept this statement as of general validity. The rolled zinc tested by Moore was not representative of the high ductility which can be obtained in this product.

Briefly, the author has annealed and examined a series of samples which had previously been severely strained in a vise, using a set of five annealing temperatures between 66° and 360° C. inclusive.

The chemical composition of the metal is not given. An admirable set of photomicrographs is included but statement of the magnifications used is overlooked.

The author was very careful in his preparative technique to keep the metal cooled by means of ice water in order to avoid structural changes during such handling.

A rather lengthy period of anneal, viz., 6 hr., was used in the tests. The result, as exhibited in the micrographs, is similar to that which has been described so often in the case of brass and other copper base alloys; a definite grain size corresponds to each annealing temperature and growth of grain is very perceptible from one temperature stage to another. The author observes, however, that the grain size is not determined by the temperature in the sense that an equilibrium value is obtained for each temperature. For example, continued annealing of the 302° C. sample for two weeks produced a striking increase in its grain size.

He also reports coarsening at room temperature of a sample which had been worked 15 years previously.

Good illustration is given of the structural effect produced in the grains by shock or slight working. Even very moderate strains, such as may easily result in removing a casting from the mold, usually suffice to alter the structural appearance by causing bands ("raies") of varying width, direction, and hue to bridge or partly cross individual grains.

We may add that any bending or similar manipulation of a coarse-grained piece of rolled zinc will bring about the same effect and that this structural alteration is contemporaneous with the "cry" which accompanies the strain. This effect can be distinctly recognized as a change of orientation of narrow blocks of material within the grain and there seems to be little doubt that it is a form of mechanical twinning. It is noteworthy, however, that worked zinc which has subsequently been annealed and rendered coarsely crystalline shows no evidence of the twinned structures which are so common in annealed brass and copper.

Timofeeff writes that in the early stages of an ordinary process of deformation the contours of the large grains, each permeated by these "raies," can be distinguished, but that at the end the totality of metal is transformed into a mass of small crystals showing a longitudinal distribution in accordance with the principal direction of extension of the piece.

"The greater the number of gliding planes and the smaller the size of the crystals, the greater the ease of working the metal."

Our own annealing experiments with strip zinc have produced results which seemed rather surprising in view of Timofeeff's regular and even

growth of grain from one annealing temperature to another, *i.e.*, we could obtain no sharp control over the grain size in annealing, as the phenomenon of selective grain growth seemed to predominate more or less in accord with certain generalizations advanced by Jeffries.[3]

During the last three (war) years two foreign papers of considerable interest in the zinc field have appeared:

(5) E. H. Schulz. Neuere Erfahrungen über Wege zur Veredelung des Zinks. *Metall. und Erz.*, vol. 13 (H.F.4) Heft 12 (1916) pp. 279–289.

(6) L. Guillet and V. Bernard. Recherches sur des Alliages Riches en Zinc. *Revue de Métallurgie*, vol. 15 (1918), pp. 407–425.

Our review of the technical literature in this field will be concluded with a brief summary of these two papers.

Schulz's paper contains no lengthy tables of data but deals in a more general way with the properties of (1) unalloyed and alloyed products in cast form and (2) unalloyed and a few alloyed products as drawn or extruded.

The author proceeds from the point of view that wrought zinc has in no way attained to a position of importance commensurate with the large production of the metal (in Germany and Belgium). He observes that there are two possible methods of "ennobling" or improving the qualities of a metal, viz., by alloying, and here he cites the alloy-steels as an illustration, and by thermal and mechanical treatment.

There follows a description of the effects of iron, tin, aluminum and copper in various percentages up to five or six on the grain characteristics (by fracture), the Brinell hardness, the tensile strength and elongation, and the transverse (bending) strength of zinc.

The material used as a starting point for these tests was the German "Raffinadezink" containing up to 1.3 per cent. of lead and 0.2 per cent. of iron, some cadmium, and traces of other metals.

The author states that such material as cast in forms is rather coarsely crystalline, brittle, 39-hard according to the Brinell test and 13 according to the Shore test, and of low strength (3000 to 4000 lb. per sq. in.), and practically no ductility in the tension test. While chiefly by pouring just above the freezing temperature, its grain may be not inappreciably improved (refined), nevertheless, the limitations are such that alloying is a very logical procedure to adopt.

As a result of alloying, improvement in practically every property except that of ductility was attained.

Relative to the effects of the different metals, iron and tin produced no improvement, while aluminum and copper appeared in a more favorable light.

Six per cent. of the former metal raised the tensile strength of "Raffi-

[3] Various papers and discussions on Grain Growth published in the *Transactions* for the years 1916–17.

nadezink" up to some 23,000 lb. per sq. in. and intermediate quantities produced intermediate effects. The hardness of the alloy containing 4½ per cent. of aluminum was 72 Brinell and 29 Shore and the cross-bending strength of this alloy was more than 1 kg. per mm². as compared with 0.4 kg. per mm². for the unalloyed metal. Considerable toughness is also attributed to these aluminum alloys. In spite of these favorable properties, the author advocates caution with respect to the use of aluminum in zinc. He bases this mainly on conclusions drawn from one of the old zinc-aluminum diagrams according to which about 3 per cent. of aluminum can exist in solid solution in zinc. Beyond 3 per cent., in addition to the zinc-rich solution, a second structure element containing some 50 per cent. of aluminum appears and it is the segregation of this lighter constituent which the author fears when moderately large quantities of aluminum are added to zinc.

This conclusion should be modified in the face of newer and much more complete equilibrium data supplied by Bauer and Vogel,[4] viz., less than 1 per cent. (instead of 3 per cent.) of aluminum dissolves in solid zinc and the second constituent contains scarcely more than 20 per cent. of aluminum (instead of 50 per cent.), whereby the net tendency to segregation would probably be lessened.

However, in addition to this more or less theoretical evidence, the author cites a practical disadvantage of aluminum, in that it tends strongly to promote unsoundness in the castings. For these various reasons the author prefers to use not more than 3 per cent. of aluminum in zinc.

This question of the effect of aluminum in zinc is one which seems to require additional consideration and it may not be amiss to point out at this time another aspect of the situation. As will be shown later, Guillet has also ascribed very favorable tensile properties to zinc alloyed with aluminum, and his tests were made with worked material (both rolled and drawn). In fact, in reading the literature one cannot avoid the impression that aluminum, or aluminum in combination with copper, when alloyed with zinc produces a superior type of material, at least from the standpoint of mechanical properties.

On the other hand, we can refer very positively to cases of failure due unmistakably to the presence of aluminum in the metal. Such failures are of the nature of weakening or even disintegration under extreme atmospheric conditions, or similar effects in greatly exaggerated form under artificially induced conditions such as exposure to wet steam. Rigg and Morse[5] have reported exposure experiments using steam at

[4] Beitrag zur Kenntnis der Aluminium-Zink-Legierungen. *Internat. Zeitschr. für Metallog.* (1916) 8, 101–178.

[5] Effects of Impurities in Spelter on Slush Castings. *Trans.* Am. Inst. Metals (1915) 9, 53.

ordinary atmospheric pressure with cast zinc-aluminum alloys containing a rather high percentage of aluminum (20 per cent.) and made from various grades of spelter. They encountered cracking, swelling, and even crumbling in the case of those alloys made from common spelter, while no such results occurred in the case of alloys made from high-grade spelter. Failures of zinc-base die castings containing aluminum have been reported a number of times and yet in a recent test we exposed a thin walled die-casting containing (6–6½ per cent. tin, 2½ per cent. copper, and ½ per cent. aluminum) to steam for more than a week without sensible alteration.

We have, however, a record of remarkable failures in the case of zinc foil (0.008 in. thick) rolled in the laboratory from seven small castings containing from 0.01 to 0.5 per cent. of aluminum. After a 24-hr. treatment in wet steam, all of these except the first became noticeably brittle and those containing only a few hundredths or a few tenths of a per cent. of aluminum had blackened, blistered, swollen, and in general become so brittle that they broke in mere handling.

Similar tests were made with foil containing various additions of lead, copper and cadmium (separately) but brittleness of this sort was not encountered in any case.

Further tests were made on thin zinc strip rolled according to the usual practice in the mill from Horse Head slabs alloyed so as to contain 1 per cent. of copper + 1 per cent. of aluminum, 1 per cent. of copper + 2 per cent. of aluminum, and 3 per cent. of copper + 1 per cent. of aluminum. All of this material blackened, swelled, and became brittle. A few tests were then made with an aluminum alloy prepared from a sample of extremely pure zinc. The failures again occurred but in less pronounced form than was the case with less pure alloys of similar composition.

It seems fairly evident that the deterioration of these alloys is primarily a specific property of the binary system zinc-aluminum within certain concentration limits *on the zinc side*, but that the presence of certain impurities accelerates the action.

Bauer and Vogel's equilibrium diagram indicates two possible explanations:

1. That it is due primarily to the chemical action of water-vapor on the compound, Al_2Zn_3, present in these alloys.

2. That it is due to volume changes associated with the transformation of the compound into the two solid-solution phases (saturated zinc-rich solution containing 0.75 per cent. Al + saturated aluminum-rich solution containing 25 per cent. zinc) which occurs at 256° C.

While we cannot go into this matter exhaustively, the fact that heat treatment alone does not produce disintegration and the additional fact that in cases of half-way or uncompleted disintegration perfectly good material is found in the interior of the sample (*i.e.*, the action pro-

ceeds from the surface inwards) determine our preference for the first explanation.

In order to avoid any possible misconception as to the general behavior of zinc and aluminum in combination, it should be emphasized that the disintegration just described does not occur, nor would it be expected, in the case of alloys containing very high percentages of aluminum. For example, the compound Al_2Zn_3 does not occur in an alloy composed of 80 per cent. aluminum + 20 per cent. zinc, but the zinc remains in solid solution in the aluminum. An alloy of this sort behaves well in comparison with commercial aluminum when subjected to corroding influences. Any one interested in this subject will find much valuable information in Bauer and Vogel's paper.

Returning again to the discussion of Schulz's paper, we note that his tests of the copper alloys likewise indicate considerable improvement in the mechanical properties. There is a gradual increase in hardness with the copper content and likewise a gradual increase in strength. For example, the 1 per cent. alloy has a Shore hardness of 16 and a tensile strength of about 8500 lb. per sq. in., while the 4 per cent. alloy has a hardness of 27 and a tensile strength of about 18,500 lb. per sq. in. Furthermore, it is stated that copper is effective in refining the grain of cast zinc.[6] Except for a certain type of shortness ("Kurzbruchigkeit") with the higher copper contents, the author finds copper the most suitable material to choose for the purpose of improving the quality of cast zinc. He thereupon proceeds to utilize the toughening property ascribed to aluminum, by combining the previously specified limiting quantity of 3 per cent. of this metal with enough copper to raise the tensile strength to the desired value.

Thus, a zinc alloy containing 3 per cent. of aluminum and 2 per cent. of copper gives a tensile strength of about 10,000 lb. per sq. in. while one with 3 per cent. of aluminum and 6 per cent. of copper gives nearly 26,000 lb. per sq. in. It is stated that these alloys can be poured so as to produce a fine grain and that they have no pronounced tendency to unsoundness.

The latter alloy virtually represents the outcome of the author's efforts to produce a highly improved cast zinc. He considers that it compares with the more expensive copper-brass alloys very much in the same way that cast iron compares with steel, *i.e.*, it is described as an eminently suitable material for many purposes, although perhaps not adapted to general use as a material of construction.

The last part of Schulz's paper deals with the improvement of zinc by mechanical and thermal treatment, viz., by rolling, drawing, and extruding, chiefly the latter.

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[6] We have not found this to be strictly the case in our own experiments using Horse Head spelter as a base.

The process of rolling is cited merely as a well-known example of the efficacy of thorough working at suitable temperatures in bringing about far-reaching improvement of the properties of the metal. "As a result of this rolling into sheet, when conducted properly, the metal zinc, ordinarily so weak and brittle, becomes transformed into a material possessing a tensile strength of 27,000 to 35,000 lb. per sq. in. and a percentage elongation of 15 to 18."

The properties of good extruded zinc (presumably "Raffinadezink") are summarized as follows:

Yield point faintly marked at about 17,000 lb. per sq. in.

Ultimate tensile strength at 23,000–26,000 lb. per sq. in.

Percentage elongation (100 mm.?), 20–60.

Brinell hardness, 40–50.

Precautions as to soundness of the billet, temperature of extrusion and relation of size of billet to size of extruded rod are essential in order to attain the above desirable characteristics.

On heating an average sample of extruded rod, coarse crystallization occurs rapidly at a temperature in the neighborhood of 180–200° C., and slowly at somewhat lower temperatures. The author concludes that extrusion in this temperature region will produce inferior metal and the properties of a sample of this sort are reported as follows: ultimate tensile strength, 16,500 lb. per sq. in.; percentage elongation, 7; Brinell hardness, 41.

The author states that it is possible by rolling in grooved rolls to produce zinc rod whose properties approximate those of extruded zinc. Thus the following properties are ascribed to rolled rod 45 to 55 mm. in diameter: ultimate strength, 20,000 to 21,500 lb. per sq. in.; percentage elongation, 20 to 35; Brinell hardness, 44 to 52.

Finally, the effect of alloying with copper has been studied in relation to both rolled and extruded zinc and the following comparisons of properties are given:

	Extruded Zinc Containing 1 Per Cent. Copper	Rolled Zinc Containing 1 Per Cent. Copper	Extruded Zinc Containing 2 Per Cent. Copper
Ultimate tensile strength, lb. per sq. in.	33,000	28,500	32,000
Percentage elongation	43	31	27
Brinell hardness	72	62	64

The paper by Guillet and Bernard describes work undertaken in the effort to produce an alloyed zinc in rolled or extruded form which would satisfactorily replace certain copper alloys. These authors enjoyed the coöperation of "La Société de la Vieille Montagne" in rolling, of "Les

Fonderies des Usines de Dion Bouton" in casting, and "La Société du Duralumin" in drawing, which established very favorable conditions for the experimental working and testing of these alloys.

Six types of material were investigated:

"(*a*) Pure zinc (Pb = 0.5) and ordinary zinc (Pb = 1.0)

(*b*) Ordinary zinc + 1, 2, 3 or 5 per cent. aluminum.

(*c*) Ordinary zinc + 1, 2, 4 or 6 per cent. copper.

(*d*) Ordinary zinc + 2 per cent. aluminum + 2, 4, 6, 8 per cent. copper.

(*e*) Ordinary zinc + 4 per cent. aluminum + 2, 4, 6, 8 per cent. copper.

(*f*) Ordinary zinc + 8 per cent. aluminum + 4 per cent. copper (German type of alloy)."

The authors' summary of tests is given in Table 5.

No adequate description of any of these tests is given. In particular we deplore the lack of information as to the details of the shock tests and the significance of the values given for resilience. The authors merely cite the type of sample and machine "Eprouvette Mesnager, mouton Guillery" used.

The extruded alloys are superior to the rolled alloys, particularly with respect to ductility. Furthermore, some alloys which could not be rolled were successfully put through the press (Nos. 9, 10, 13 and 14). No attempt was made to roll alloys 16–20 inclusive (see Table 5).

The authors sought particularly to obtain a zinc substitute for a brass showing the following properties:

Ultimate Tensile Strength, Lb. per Sq. In.	Percentage Elongation	Resilience
40,000–45,500	25–30	3–5

They were partly successful with (1) an extruded alloy containing 97.5–98 per cent. zinc (1–1.2 per cent. lead) and 1.5–2 per cent. copper, which gave an ultimate strength of 42,500–44,000 lb. per sq. in., a percentage elongation of 27–28, and a resilience of 2; and with (2) an extruded alloy containing abut 8 per cent aluminum and 4 per cent. copper, which gave an ultimate strength of 51,000 lb. per sq. in. and an elongation of 24 per cent.

Considerable attention was paid to the question of homogeneity in the extruded material. Brinell impressions were not equiaxial and the rods showed a poorly distributed longitudinal fiber.

The temperature of rolling and extrusion was, in general, 125–130° C. This was selected after rather elaborate tests of hardness and resilience at elevated temperatures; and a combination of maximum hardness

TABLE 5.—*Summary of Mechanical Tests on Zinc-aluminum-*

No. of Alloy	Composition by Analysis					Cast Alloys		
	Zn	Al	Cu	Pb	Fe	Ultimate Strength,[a] Lb. per Sq. In.	Brinell Hardness. Diam. of Impression with 10 Mm. Ball and 1000 Kg. Load	Ultimate Strength,[b] Lb. per Sq. In.
1	98.84	Trace	....	1.15	Trace	1,707	5.18–5.13	23,754
2	97.80	1.12	....	1.08	Trace	3,215	4.15–4.35	18,775
3	95.93	2.51	....	1.53	Trace	8,904	4.45–4.25	31,292
4	95.47	3.11	....	1.04	Trace	9,573	4.40–4.30	32,999
5	93.10	5.76	....	1.14	Trace	.....	4.10–4.13	33,995
6	97.95	0.07	0.85	1.10	Trace	.....	.....	31,150
7	97.52	....	1.30	1.10	Trace	5,206	4.20–4.25	32,715
8	94.67	....	4.21	1.10	Trace	10,895	4.20–4.25	43,383
9	92.36	....	6.44	1.06	0.09	17,538	3.95–4.03	.....
10	89.83	Trace	9.07	1.06	Trace	25,219	3.90–3.85	.....
11	94.79	2.01	2.00	1.27	Trace	3,499	3.65–3.65	30,297
12	93.31	2.18	3.66	0.80	Trace	15,362	3.78–3.68	45,650
13	90.85	2.23	6.01	0.85	Trace	17,438	3.55–3.50	.....
14	88.31	2.24	8.20	1.10	Trace	20,952	3.40–3.50	.....
15	99.43	....	....	0.51	Trace	2,176	5.80–6.10	20,767
16	92.60	4.45	1.89	0.98	Trace	12,232	4.01–3.81	.....
17	90.83	4.45	3.81	0.85	Trace	23,327	3.80–3.90	.....
18	88.96	4.41	5.73	0.91	Trace	22,189	3.50–3.60	.....
19	87.18	4.41	7.60	0.80	Trace	24,323	3.60–3.40	.....
20	86.60	8.53	3.85	0.98	Trace	23,754	3.47–3.40	.....

[a] Test specimens, 13.8 mm. in diam. Test section, 100 mm. long. Elongation and reduction of
[b] Test specimens, 9.4 mm. in diam. Test section, 68 mm. long.

and resilience was the criterion used to define the most favorable temperature. The curves indicate that the hardness would continue to decrease beyond the maximum temperature used (200° C.), but the resilience with most of the alloys rose rapidly from room temperature to a high value at about 100° C. which thereafter changed only slightly.

Nothing whatever was written relative to the technique of rolling or extrusion.

We have already remarked upon the striking examples of disintegration produced by aluminum in thin zinc sheet, upon exposure to wet steam. Since Guillet and Bernard have called particular attention to the favorable mechanical properties of an alloy containing 6 per cent. of aluminum in rod form we will refer again briefly to this subject.

While we have no knowledge of exposure tests made with relatively thick material of this composition, the fact that the disintegration works from the surface inwards and that even thin sheet lasts a long time in a moist atmosphere at ordinary temperature (many samples which became hopelessly brittle after 24 hr. in wet steam behaved fairly well in laboratory storage, although at the end of 6 months deterioration was plainly evident) leads us to believe that such material in rod form (with a relatively high volume to surface ratio) would not become seriously affected even after long periods of time under ordinary conditions. How-

copper Alloys, as Cast, Rolled and Extruded. (Guillet et Bernard)

Rolled Bars				Extruded Rod				
Elongation, Per Cent. in 68 Mm.	Per Cent. Reduction of Area	Brinell Hardness	Resilience (Shock Test)	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 68 Mm.	Per Cent. Reduction of Area	Brinell Hardness	Resilience (Shock Test)
34.50	79.1	5.25–5.25	1.87	29,301	30.8	66.8	4.90	2.5
1.47	4.2	4.40–4.80	1.87	.....	....	....	4.20	2.5
4.40	8.3	4.35–4.35	1.25	36,740	26.4	59.0	4.30	2.5
14.70	23.9	4.40–4.40	1.87	35,281	25.0	47.6	4.70	2.5
2.94	8.3	4.50–4.40	1.87	39,258	26.4	42.9	4.20	1.9
1.47	4.2	3.90–3.90	1.87	39,258	19.1	65.5	4.30	1.9
1.47	4.2	3.80–3.85	1.87	43,383	27.9	56.6	3.90	1.9
7.35	38.0	3.85–3.80	1.25	47,650	22.0	68.3	3.90	1.6
....	....	.....	....	51,206	10.2	14.3	4.20	1.2
....	....	.....	....	51,345	1.4	6.2	3.65	1.2
1.47	4.2	3.60–3.65	1.87	45,658	8.8	18.2	3.60	1.9
4.40	8.3	3.50–3.50	1.25	53,197	16.1	20.1	3.80	1.2
....	....	.....	....	48,788	1.4	8.3	3.80	1.2
....	....	.....	....	54,619	2.9	6.2	3.50	1.2
4.70	85.3	5.75–5.65	1.87	21,905	44.0	84.5	5.45	2.5
....	....	.....	....	46,939	16.1	22.0	3.90	1.9
....	....	.....	....	51,206	11.0	18.2	3.62	1.2
....	....	.....	....	51,206	13.2	14.3	3.55	1.2
....	....	.....	....	52,201	8.8	10.3	3.65	1.2
....	....	.....	....	50,779	24.2	39.7	3.75	1.2

area = approximately 0 in these samples.

ever, before selecting any of the zinc-rich zinc-aluminum alloys it would seem advisable to carefully consider the type of service required and until the evidence is clearer on the above point, we would prefer to advocate the use of a copper alloy as a general thing.

2. Properties and Behavior of Zinc from a Theoretical Point of View

In this section of the paper it is proposed to deal with some of the characteristics of zinc from a more or less theoretical metallographic standpoint.

It is self-evident that the properties of a metal are primarily determined by its constitution and modern metallographic research is tending more and more definitely to ascribe a form of constitution to the pure metals which gives abundant opportunity for keen speculation as to their probable behavior under different conditions. We refer to the so-called amorphous theory which in its simplest elements proposes that the crystalline grains of which a metal is composed do not come directly in contact with one another but are surrounded by a thin layer or film of metal in a non-crystalline state, and that when the crystalline grains are permanently deformed by mechanical action thin films of non-crystalline material are formed along the planes of translation or slip within the grain substance.

Thus, we must consider the properties of even the simplest metallic substance—a pure metal—with relation to the combined behavior of these two kinds of material.

So much has lately been written on the amorphous theory that we can properly refrain from any lengthy discussion of the subject. In fact, we desire only to point out some of the simple deductions from the theory which apply to zinc and for this purpose, we will make free use of

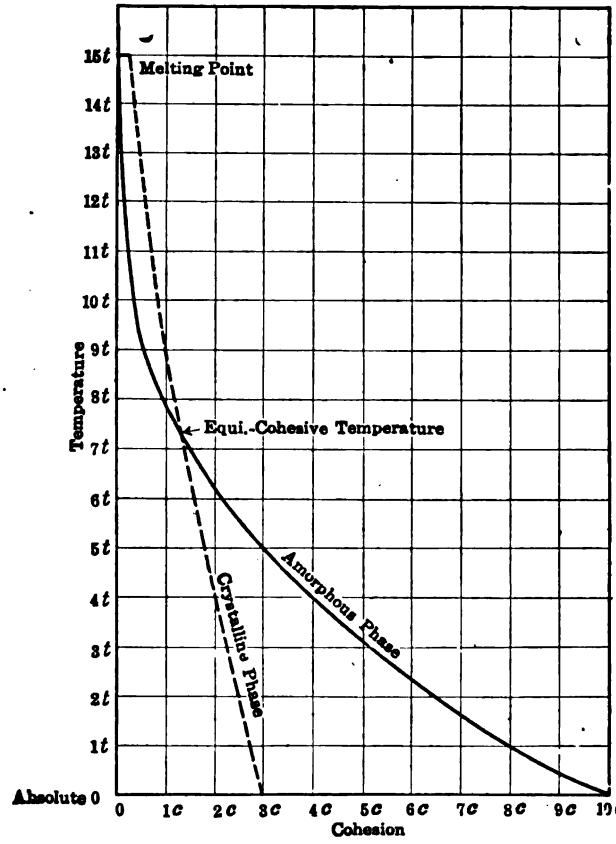

FIG. 2.—COHESION-TEMPERATURE CURVES OF AMORPHOUS AND CRYSTALLINE PHASES OF ANY METAL. (*Jeffries.*)

Jeffries' recent paper, "Effect of Temperature, Deformation and Grain Size on the Mechanical Properties of Metals,"[7] with the comment that this brings the subject quite up to date and gives the principal sources of earlier information.

A large part of Jeffries' theoretical reasoning is based on his conception of the manner in which the cohesion of the amorphous and the crystalline phases change with the temperature, as represented by the accompanying diagram (Fig. 2).

[7] *Trans.* (1919) **60**, 474.

In explanation of this diagram, we quote Jeffries[8] as follows: "The curve traced by a continuous line represents the change in cohesion of the amorphous phase with change in temperature. The cohesion is substantially zero at the melting point of the metal and increases as the temperature decreases, reaching a maximum at absolute zero. The dotted curve represents the change in cohesion of the crystalline phase with change in temperature. The crystalline phase disappears and changes into the amorphous phase when the metal is melted. On cooling from above the melting point, the crystalline phase forms during solidification and immediately at the melting temperature its cohesion assumes a finite value many times greater than that of the amorphous phase at the same temperature. On cooling below the melting point, however, the crystalline phase increases in cohesion at a very much slower rate than the amorphous phase. At some temperature between the melting point and absolute zero (in most metals not far from 0.35 to 0.45 of the absolute melting point) the cohesion of the crystalline phase will be the same as that of the amorphous phase. This temperature I have called the 'equi-cohesive temperature.' It corresponds in most, if not all, metals, to the lowest equiaxing temperature of the severely cold-worked metal. Just as the equiaxing temperature of the metal is increased with decrease in the time of heating, the apparent equi-cohesive temperature increases as the time of applying the load by which the cohesion is measured is decreased. If a metal is deformed above the equi-cohesive temperature and kept at that temperature, the grains will not remain permanently deformed, but will equiaxe; the properties of the metal will be different after equiaxing. If, however, the grains are deformed below the equi-cohesive temperature, they will remain permanently distorted. Below the equi-cohesive temperature, the amorphous phase has not only greater cohesion than the crystalline phase but its cohesion increases much faster with decrease in temperature."

As noted above, Jeffries has discovered that the temperature of equal cohesion of the crystalline and amorphous phases is virtually identical with the earliest temperature of recrystallization from a strain-hardened condition. This makes it comparatively simple to determine this important temperature, or at least to get a good idea of its approximate location.

Without describing in detail the author's handling of his experimental material, we may state that his explanation of the properties determined at various temperatures with copper, iron, and tungsten after deformation at various temperatures, constitute a most convincing demonstratio n of the validity of the principal theoretical contentions.

In particular, he arrives readily at an explanation of the increase in

[8] The Metallography of Tungsten. *Trans.* (19 19) **60**, 622.

ductility of copper wires, first discovered by Beilby, which is obtained by testing at low temperatures after drawing at higher temperatures.

This behavior apparently classes under a generalization that the strength and ductility of material worked below the equi-cohesive temperature will increase as the temperature of test decreases below the temperature of cold-working.

This particular point has not been tested out in the case of zinc and it is relatively of less importance in the zinc field than in most other branches of metal-technology because the normal range of working zinc lies at or close to the equi-cohesive temperature instead of far below it as in the case of copper, brass, etc., and this temperature is not far above the temperature of application of the metal as imposed by natural circumstances. Thus we cannot make use of the improved properties which might result from working zinc just below the equi-cohesive temperature and using the metal far below the temperature in question.

The general bearing of the location of the equi-cohesive temperature on the properties of metals seems to be of the utmost importance. If the temperature is below the atmospheric temperature, as in the case of lead, the familiar and useful type of hardening and strengthening by strain (mechanical working) cannot take place because spontaneous recrystallization will occur. Apparently we know no metals in which the crystalline and amorphous values of cohesion are both very high and equal at low temperatures. The tendency of the grain fragments in a strain-hardened metal to coalesce and grow under the influence of crystallographic forces and perhaps surface tension, while specific in any given material, seems to be of about the same general order of magnitude in the different metals, so that it overcomes the rigidity of the enveloping amorphous material when the latter reaches a certain degree of plasticity; which may occur at a very low temperature, as in the case of lead, or at an extremely high temperature, as in the case of tungsten.

In the case of zinc, it occurs at a moderately low temperature and from the nature of the properties entailed, we believe that this temperature of equal cohesion in the case of zinc occurs at a relatively high value of specific cohesion.

In other words, the strong crystallographic forces in zinc are able to operate against relatively rigid amorphous envelopment. Practically considered, this would determine a high degree of usefulness in the sense that in spite of a low temperature of recrystallization and equal cohesion a fair amount of strain hardening should be possible within the limited temperature region available for cold working.

Thus, we have raised the tensile strength from 20,000 lb. per sq. in., its value in annealed (coarsened) material up to nearly 40,000 lb. per sq. in. in the case of thin samples rolled from common spelter (tested across the grain).

The following may be said relative to the location of the equi-cohesive temperatures in pure zinc and alloyed zinc:

We have made hundreds of annealing tests on zinc to which practically all of the ordinary metals have been added singly and in many forms of combination up to low values of concentration, such as would permit practical rolling of the product. In these tests, carried out primarily for the purpose of determining the softening characteristics of different kinds of alloyed zinc, slabs ¼ in. thick were broken down hot in laboratory rolls to a thickness of about ⅛ in. and then finished with water-cooled rolls using very light reductions to avoid heating to a final thickness of 0.020 in. The softening characteristics were fully investigated by annealing for periods of 5, 15, 30, 60 and 300 min. and 1 week at the temperatures; 50°, 75°, 100°, 125°, 150°, 200°, 250°, 300°, 350° and 400° C. The scleroscope furnished a convenient and rapid means of following the softening characteristics.

The presentation and analysis of this mass of data would require altogether too much space but some pertinent conclusions may be offered, viz.:

Very pure zinc (containing 0.004 per cent. of lead and 0.005 per cent. of iron) cannot be rolled at room temperature so as to retain any appreciable amount of strain hardening. As the rolling progresses, the casting grain gradually becomes refined quite according to the early succession of structures shown in Plate II although this illustration is taken from a common grade of metal broken down hot according to the universal practice in zinc rolling mills. At the finish the metal possesses a rather fine equiaxed grain which is illustrated in Fig. *A* of Plate I. (The grain diameter is in the neighborhood of 0.02 mm.).

If precautions are taken to keep the metal and the rolls cold, the rolled sheet will show an increase in hardness of a few Shore units above that of fully annealed metal.

The above observations do not indicate that the recrystallization- or equi-cohesive temperature is below room temperature, say 20° C., because there must be some internal heating of the metal during rolling, so that the equiaxed structure is produced at a temperature somewhat above this value. Annealing tests check this conclusion, as softening on anneal begins at some 40° or 50° C. and short or long periods of anneal produce about the same effect.

The equi-cohesive temperature of pure zinc is thus in the neighborhood of 40° C.

Practically all metals raise the equi-cohesive temperature of zinc even when added in very small quantities, *i.e.*, amounting to tenths of a per cent. This may not be manifested in the form of an elevated softening temperature but it is at least evident in the increased hardness of the rolled sheet.

The precise effects of the different elements vary in this respect. Thus, lead alone gives a harder sheet which softens at low temperatures; cadmium gives a very much harder sheet which also softens at low temperatures but in a measure is considerably dependent upon the period of anneal; the metals of the iron group widen the range of softening necessitating quite high temperatures for a full anneal; magnesium is very effective in hardening and raising the softening temperature but it also seriously embrittles the sheet; copper is effective in raising the hardness and also in raising the softening temperature when present near the limit of its solid solubility in zinc (some 2 per cent.); the hardening effect of aluminum is later offset by (chemical) softening and disintegration as previously pointed out.

Sheet rolled from a common spelter containing, say 0.75 per cent. of lead, 0.33 per cent. of cadmium and 0.01 or 0.02 per cent. of iron will show a Shore hardness of 30, as against 15 for the very pure zinc and will require more than a week for a full anneal at 100° C. Its equi-cohesive temperature in all probability lies 50° C. above that of the pure zinc.

Since the equi-cohesive temperature of pure zinc is not far above room temperature, *i.e.*, the temperature at which the metal must stand service, and since this condition makes it impossible to maintain the metal in a strain-hardened condition without keeping it artificially cooled, we must turn to an impure or alloyed zinc, possessing a higher equi-cohesive temperature, if we desire to roll permanent temper into the metal. Thus, from a practical point of view, the most important effect of alloying on zinc is the possibility which it opens of hardening the metal more or less as copper, brass, etc., are hardened by cold working. The possibilities are, indeed, limited in this respect, but sufficiently marked to be of use. More information on this subject will be given in the later sections of this paper.

Another characteristic of zinc which can be most readily appreciated when reviewed from the standpoint of the amorphous theory is its capacity to yield more readily under slowly applied stresses than under rapidly applied stresses.[9] The amorphous phase in a metal not far removed from its equi-cohesive temperature, *i.e.*, in zinc at atmospheric temperatures, is conceived to be of a plastic nature. While it might readily yield under a steadily applied stress and permit the enclosed crystals to deform it would be more resistant to the same stress applied more rapidly just as pitch or heated glass would behave under similar circumstances. At lower temperatures its internal friction increases and it becomes stiffer, however the load is applied.

A general effect of alloying is to stiffen the amorphous phase so that

[9] Cf. Martens, Meyer and other authors reviewed in the first part of this paper.

plastic flow is less pronounced under the same temperature conditions. A good illustration of this is seen in the stress-deformation curves of Fig. 14. The Horse Head rod (No. 1) stretches more under a given stress applied at a given rate than the alloyed rods, all tested at room temperature, which, however, is nearer the equi-cohesive temperature in the case of Horse Head rod than in the case of the other rods. A brass rod would

FIG. 3.—APPARATUS FOR TENSILE TESTING AT ELEVATED TEMPERATURES.

stretch less under the same conditions primarily because it would be still further removed from its equi-cohesive temperature. Here the effect of rate of loading would become prominent only in tests at elevated temperatures.

Stiffness is as a rule a desired property in rod material and pure zinc is therefore likely to be less satisfactory in this respect than alloyed or impure zinc. The conditions may be quite different in the case of metal intended for press work. Much data will be given in a later section on the effect of rate of forming cups of the Erichsen type using different

kinds of zinc. Here, Horse Head metal has shown a decided superiority over all other types tested.

Considerable interest is attached to the behavior of metals when tested at elevated temperatures. We have already referred to tensile data of this sort in the case of zinc.[10] Similar tests have been made in the Palmerton laboratory. Two kinds of material were used (1) a common zinc containing, by analysis, 0.37 per cent. of lead, 0.016 per cent. of iron and 0.04 per cent. of cadmium; (2) a relatively pure zinc containing 0.065 per cent. of lead, 0.018 per cent. of iron and no cadmium. Both metals were in a strain-hardened condition, the former showing a scleroscopic hardness of 27 and the latter 23–24. Photomicrographs of the respective samples are given in Figs. *B* and *C* of Plate I.

A photograph of the set-up used in these tests is given in Fig. 3. Very little description is necessary to make this clear. The furnace contained a wire-wound electric heating element with windings spaced so as to give a flat thermal gradient, and considerable heat insulating packing between this and the outside shell. The test specimen was about 15 in. long, the central two-thirds of which was located in the furnace tube at the start of the test. The hot junction of the carefully calibrated thermocouple was fixed in contact with the specimen as shown. The cold junction, wrapped around the bulb of the thermocouple, was kept in a thermos bottle.

TABLE 6.—*Tensile Data from Tests on Zinc Strip at Elevated Temperatures*

(*Average of three to six tests*)

	No. 1 Strip (Common) 0.055 In. Thick				No. 2 Strip (Horse Head) 0.055 In. Thick			
	With Grain		Across Grain		With Grain		Across Grain	
Temperature, Degrees C.	Ultimate Strength, Lb. per Sq. In.	Percentage Elongation in 2 In.	Ultimate Strength, Lb. per Sq. In.	Percentage Elongation	Ultimate Strength, Lb. per Sq. In.	Percentage Elongation	Ultimate Strength, Lb. per Sq. In.	Percentage Elongation
28	.....	....	.....	....	20,575	78.9		
23	29,862	42.5	.....	....	.....	....	28,200	41.2
25	.....	....	38,800	31.2				
50	26,067	47.3	30,675	34.5	15,700	63.8	21,850	53.2
75	22,162	51.7	24,825	37.4	13,000	63.0	17,417	46.5
100	17,383	67.2	19,760	39.4	10,800	68.2	15,000	50.5
110	.....	....	.....	....	11,120	71.2	14,175	46.7
115	16,675	68.6	.....	....	10,150	76.6	14,600	41.5
125	14,233	78.2	17,925	41.0	9,986	67.6	15,150	34.4
130	12,400	81.0	15,622	43.9				
135	13,967	78.3	15,312	32.6	9,975	55.7		
140	11,025	68.7	15,375	45.1				
145	.....	....	14,380	29.3	8,905	54.0		
150	11,475	69.6	15,800	33.6	8,587	53.4	13,520	22.6
160	.....	....	.....	....	8,265	50.7		
175	9,714	47.7	14,500	20.8	8,400	48.1	13,375	23.2
200	9,343	41.9	13,300	19.0	6,610	45.0	10,400	19.1

[10] Data supplied by Martens is given earlier in this paper (see Table 3).

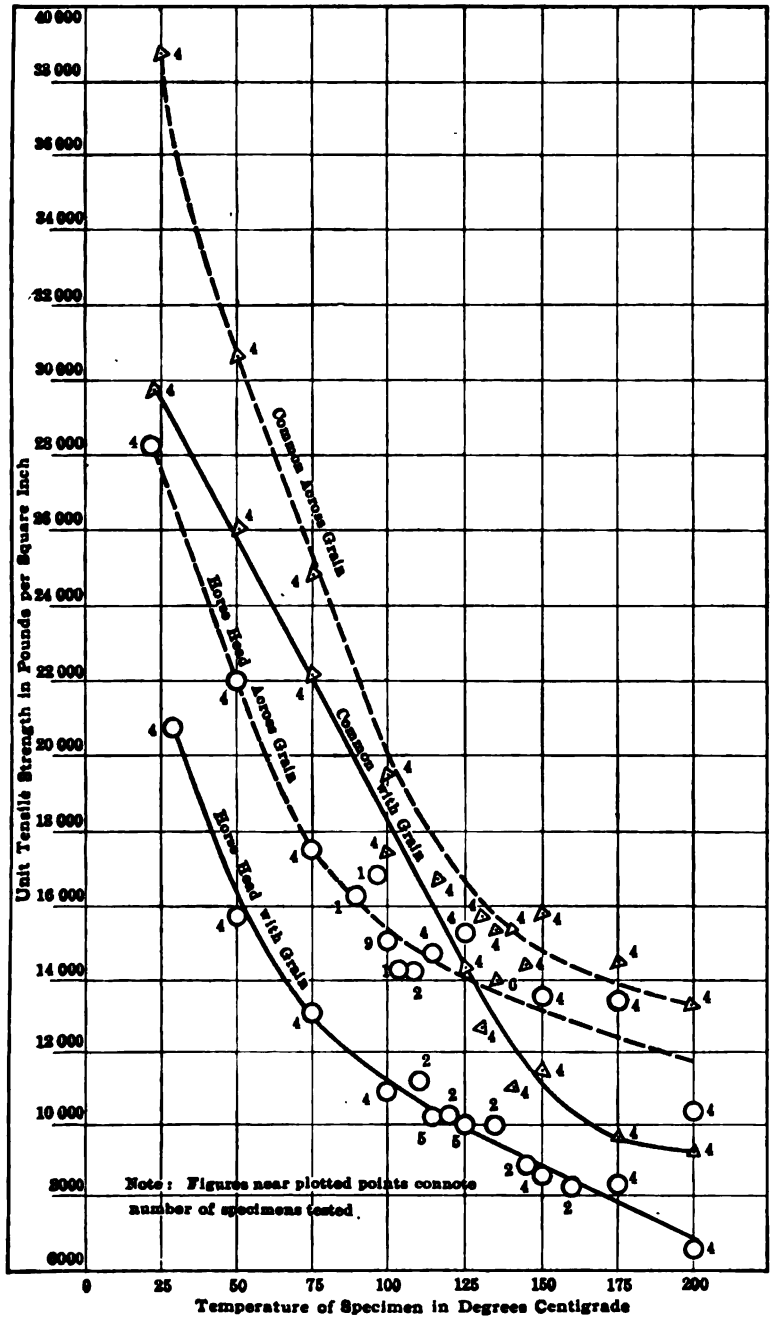

FIG. 4.—TENSILE STRENGTH OF ROLLED ZINC AT ELEVATED TEMPERATURES.

Specimens were milled in the center to give a test section ½ in. wide and a little more than 2 in. long. The material tested was 0.055 in. thick. Heating of the specimens to the desired temperature before pulling required from 5 to 15 min., depending upon the temperature. The pulling speed was 0.285 in. per min. The results are given in Table 6.

Curves showing the change of strength and elongation with the temperature may be seen in Figs. 4 and 5, respectively.

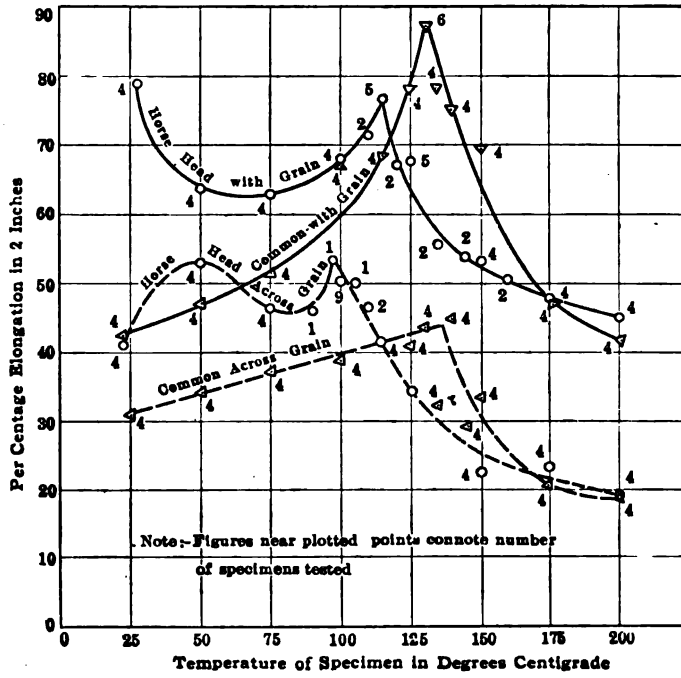

FIG. 5.—DUCTILITY OF ROLLED ZINC AT VARIOUS TEMPERATURES.

It is observed that the strength of both kinds of zinc decreases throughout the temperature range of testing. This would be expected on the ground that both the amorphous and the crystalline phases decrease in cohesion as the temperature increases. The fracture is transcrystalline throughout the series, showing that even at the higher temperature, 200° C., the cohesion of the amorphous metal has not decreased sufficiently to cause fracture at the grain boundaries under the given conditions of loading.

There is a perceptible change in the rate of decrease of strength with the temperature at about 100° C. in the case of the Horse Head material and somewhat higher in the case of the less pure material. This doubtless has to do with recrystallization in the metal during the test.

Turning to the temperature-elongation curves, we observe that the change in this temperature region is much more pronounced. Thus, the

elongation, in general, increases with the temperature owing to increasing plasticity as long as the amorphous material can be freely formed by a breakdown of the grain substance during the test, reaching its maximum just below the point where spontaneous recrystallization can first occur in the severely deformed (highly stretched) material but thereafter decreasing to correspond with the tendency for recrystallization to occur at an early stage of deformation (after moderate stretching) if the temperature is high enough, *i.e.*, the lower the degree of deformation, the higher the recrystallization temperature.

The conditions for high static ductility in zinc are: (1) Uniformity of quality (absence of segregation of impurities), (2) very fine grain or amorphization to a high degree, (3) a moderately elevated temperature.

We take exception to the conclusions of earlier authors that the maximum ductility and low strength shown in the tensile test at some 100°–150° C. are proper criteria to use in specifying the best conditions for all sorts of working. Thus, there is no point in raising the temperature of zinc to get extremely high ductility at a sacrifice of strength if the operation in hand requires the metal to resist high stresses while changing its form as in deep drawing operations. In reality, the results of the static test have little bearing on such questions as will be pointed out in a later section of this paper.

3. Effect of Ordinary Rolling Variables on Zinc as Compared with Copper and Copper-base Alloys

The following quotation from Jeffries[11] will serve as an introduction to this subject. It represents a normal transition from theory to practice and summarizes what a metallographist would be inclined to consider the vital element underlying the commercial working of zinc: "Cast zinc, or worked zinc made coarse grained by a high temperature anneal, may be brittle at room temperature and workable at 150° C., and after this working the ductility at room temperature will be greater than before working. It is now known that this increase in ductility of zinc is due to a substitution of a fine-grained structure for the coarse-grained one. It is known that 150° C. is above the annealing temperature of worked zinc and consequently in the hot working region. The refinement of the grain in zinc by working at 100° to 150° is analogous to the breaking down of the coarse grains in a steel ingot by working above a red heat."

Perhaps we should add, although this has also been well enough brought out in the contemporaneous literature, that coarse-grained zinc is specifically brittle because a crystal tends to separate along a cleavage plane when called upon to bear stress operating unfavorably against it, and that fine-grained zinc is not brittle because of intergranular reinforce-

[11] *Trans.* (1919) **60**, 594.

ment with more or less plastic amorphous material and because of the support which any unfavorably located crystal derives from its numerous neighbors, otherwise orientated, and hence capable of withstanding the stress in question.

This condition carried to an extreme would render the metal conglomerate practically isotropic, *i.e.*, its properties would be quite independent of any directional element in the method of testing. This is exactly the explanation commonly accepted to account for the superior shock-resisting qualities of a steel casting in which the grain has been refined by heat treatment as compared with a casting in its untreated (coarse-grained) form.

Coarse-grained copper and brass do not manifest this form of weakness; because the crystal slips or slides rather than parts along a cleavage —or more properly slip-plane—whatever the intensity, direction, or rate of application of the stress (within reasonable limits).

Fine-grained zinc is also characterized by movements of slip, rather than cleavage, under all ordinary conditions of deformation or loading, *i.e.*, it is a useful material in the same sense that copper and brass are useful materials.

We may add here that its highest degree of utility in this sense is attained when the average grain diameter measures 0.02–0.04 mm. This is the order of grain size obtained in pure $^{68}/_{32}$ brass by annealing at 450° to 550° C. after hard rolling.[12] Brass usually shows its best drawing properties when somewhat coarser grained than this, *i.e.*, after anneal at a higher temperature.

As the grain size of zinc increases beyond the upper limit given above, the characteristic "cry" can be detected by sharp bending (or shearing) close to the ear. This "cry" may be utilized as a rough test to indicate poor drawing characteristics. The "cry" can be heard without difficulty in rather undesirably coarse-grained sheet.

The process of rolling strip zinc is, in its mechanical features, similar to the familiar process of rolling a flat brass bar ultimately into a long coiled strip of thin metal.

The same variables come into play, viz., soundness of the casting, rolling reductions and number of passes, speed of operating the rolls, lubrication, surfacing of rolls, continuity, and efficiency of handling, etc.

In addition, the question of temperature is important and for the best results rigorous control of these various factors in their relation to one another is far more important than in the rolling treatment of brass.

There are these important differences between the rolling of zinc and of brass, for example:

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[12] W. H. Bassett and C. H. Davis: A Comparison of Grain-size Measurements and Brinell Hardness of Cartridge Brass. *Trans.* (1919) **60**, 428.

In the latter case, a wide range of temper can be obtained simply by varying the degree of cold reduction after the last anneal, viz., the tensile strength may be more than doubled whereby the percentage elongation falls from a high value to almost nothing.

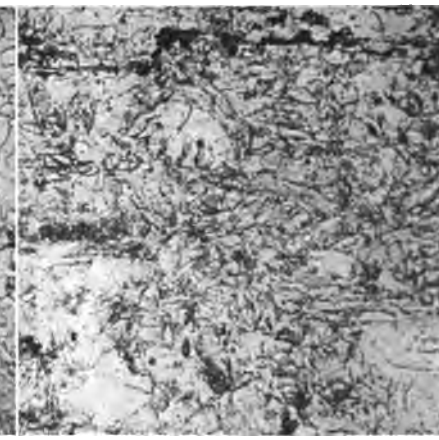
In the former case, the possibilities of varying the temper in this way are much more limited. We find it desirable to divide this product simply into two classes; hard-rolled strip and medium hard-rolled strip. The hard-rolled strip will show a tensile strength as high as 40,000 lb. per sq. in. (minimum in a test specimen cut parallel to the direction of rolling and maximum in a specimen cut at right angles to the direction of rolling). The medium hard-rolled strip will test in the neighborhood of 30,000 lb. per sq. in. There is no such drop in elongation as occurs with brass. In fact, good hard metal should stretch from 30 to 50 per cent. in 2 in. and it is only with very impure grades of spelter that trifling values of elongation are obtained. The elongation is always greater in samples cut with the grain than in samples cut at right angles to the direction of rolling.

The microstructure of a typical specimen of medium hard-rolled strip is shown in Fig. *B* of Plate I and that of typical hard-rolled metal in Fig. *D* of the same plate.

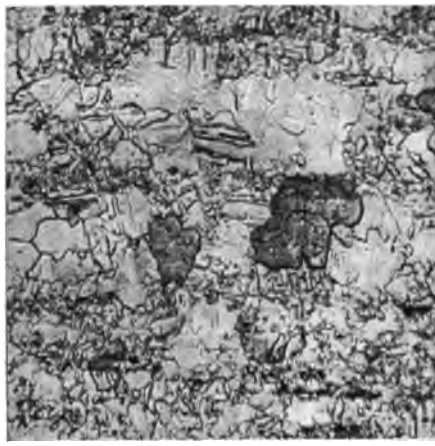
The soft tempers in brass are obtained by annealing hard-rolled metal at various temperatures between 450° and 750° C. In this way, the hard metal is softened for further rolling and the product is brought into a suitable condition of temper for a variety of cold-working operations such as deep drawing, stamping, etc. No such treatment is permissible in the case of zinc. The metal can be made structurally equivalent to annealed brass but this must be done directly by rolling, *i.e.*, the metal must leave the rolls in this condition. The structure of typical soft-rolled metal of Horse Head quality is shown in Fig. *A* of Plate I, and the structure which is ordinarily obtained in the earliest stages of annealing hard-rolled metal is shown in Fig. *E*. It is observed that very large grains have grown in places after this brief anneal of 1 min. in boiling water. The structure and drawing properties are quite different from those represented by Fig. *A* although the hardness is about the same.

From what has been written in the previous section it should be quite evident that soft rolling of different grades of zinc cannot be conducted in precisely the same manner, chiefly owing to the influence of impurities on the recrystallization temperature. Thus, we have distinguished between a soft equiaxed metal of Horse Head quality, as represented in Fig. *A* of Plate 1, and a soft equiaxed metal containing several tenths of 1 per cent. of lead. This is represented by the last figure of the plate. While the properties of these two soft strips are similar in some respects, the longitudinal banding, which is so prominent in the leaded material,

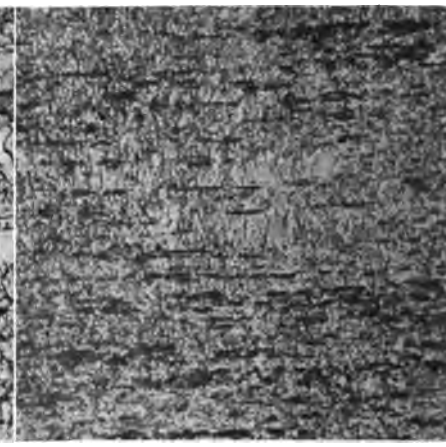
A. Dead soft-rolled strip zinc. (Horse Head quality.)



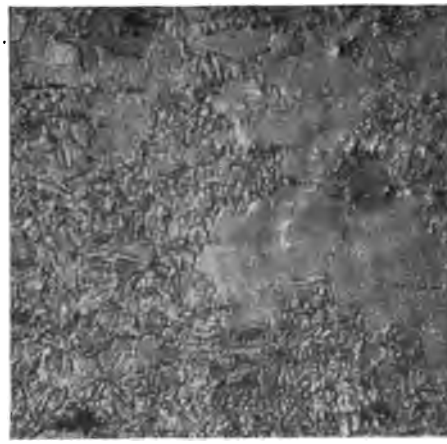
B. Medium hard-rolled strip zinc containing 0.2–0.3 per cent. lead, 0.03 per cent. cadmium and 0.01 per cent. iron.



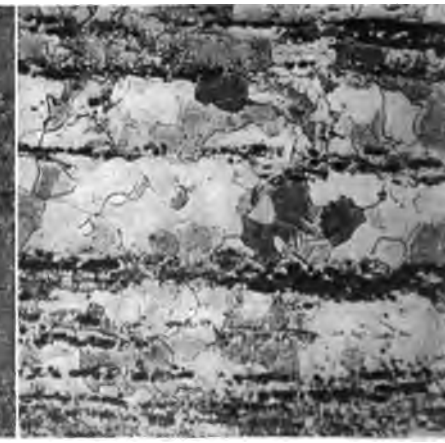
C. Medium hard-rolled strip zinc. (Horse Head quality.)



D. Hard-rolled strip zinc. Analysis as above.



E. Hard-rolled strip annealed 1 min. in boiling water.

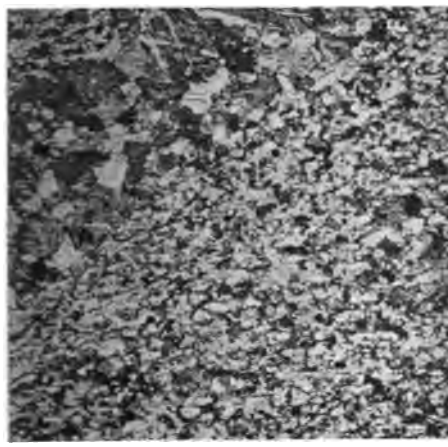


F. Soft-rolled strip. Analysis as above.

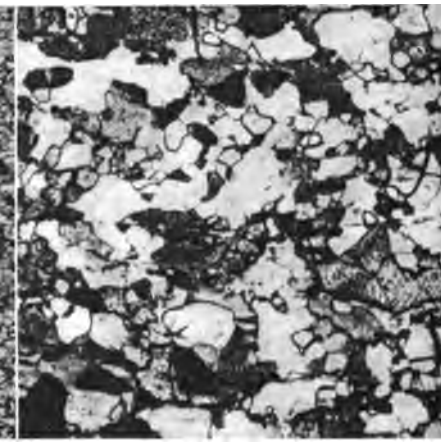
PLATE I.—STRUCTURAL TYPES OF STRIP ZINC. SAMPLES ETCHED WITH AN AQUEOUS SOLUTION OF CHROMIC ACID AND SODIUM SULFATE. × 250.

A. SLAB *A.* AS CAST. × 20.

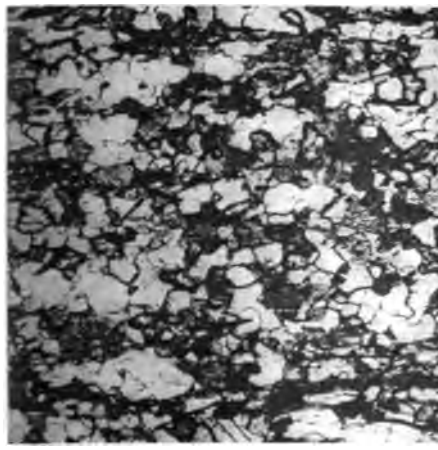
B. SLAB *B.* 15 PER CENT. TOTAL REDUCTION. × 20.



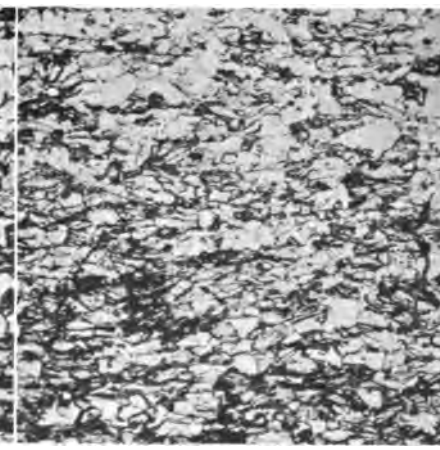
C. SLAB *D.* 37 PER CENT. TOTAL REDUCTION. × 20.



D. SLAB *D.* 37 PER CENT. TOTAL REDUCTION. × 100.



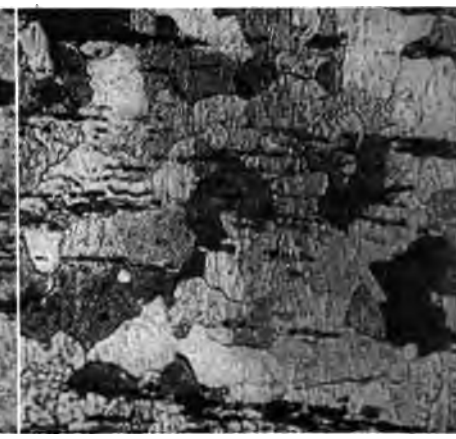
E. SLAB *G.* 85 PER CENT. TOTAL REDUCTION. × 100.



F. SLAB *H.* 87 PER CENT. TOTAL REDUCTION. × 100.

PLATE II.—GRAIN REFINING OF ZINC BY ROLLING. SAMPLES ETCHED WITH AN AQUEOUS SOLUTION OF CHROMIC ACID AND SODIUM SULFATE.

A SLAB *J*. 94 PER CENT. TOTAL REDUCTION. HARD REGION.

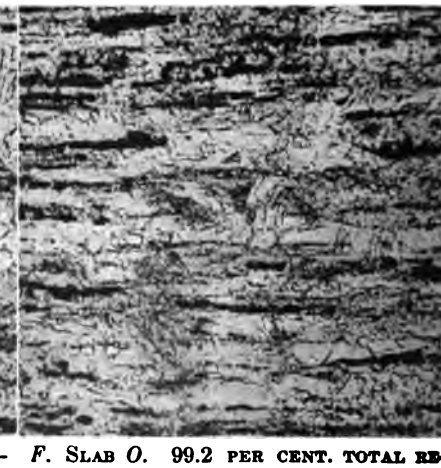


B. SLAB *J*. 94 PER CENT. TOTAL REDUCTION. SOFT REGION.

C. SLAB *K*. 95.5 PER CENT. TOTAL REDUCTION.

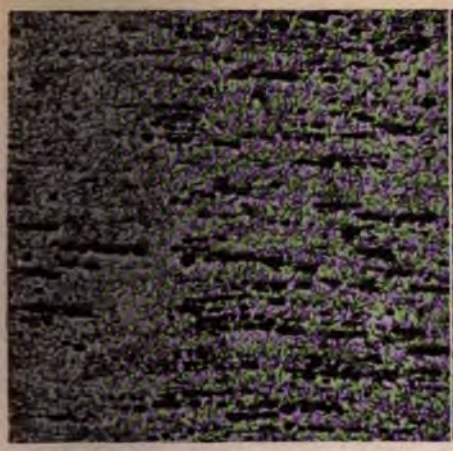
D. SLAB *L*. 97 PER CENT. TOTAL REDUCTION.

E. SLAB *N*. 98.8 PER CENT. TOTAL REDUCTION.



F. SLAB *O*. 99.2 PER CENT. TOTAL REDUCTION.

PLATE III.—HARD AND SOFT ROLLING OF STRIP ZINC. SAMPLES ETCHED WITH AN AQUEOUS SOLUTION OF CHROMIC ACID AND SODIUM SULFATE. ×250.



A. Typical of original stock and all anneals at 50 and 75° C. × 250.

B. Annealed 5 min. at 100° C. × 250.

C. × 250.

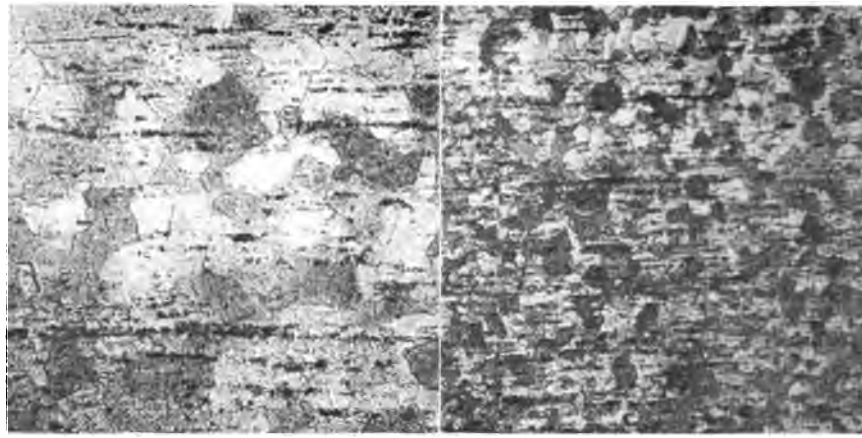
D. × 100.

Representative of 30-min., 1-hr., and 5-hr. anneals at 100° C.

E. Typical of all anneals at 150° C. × 250.

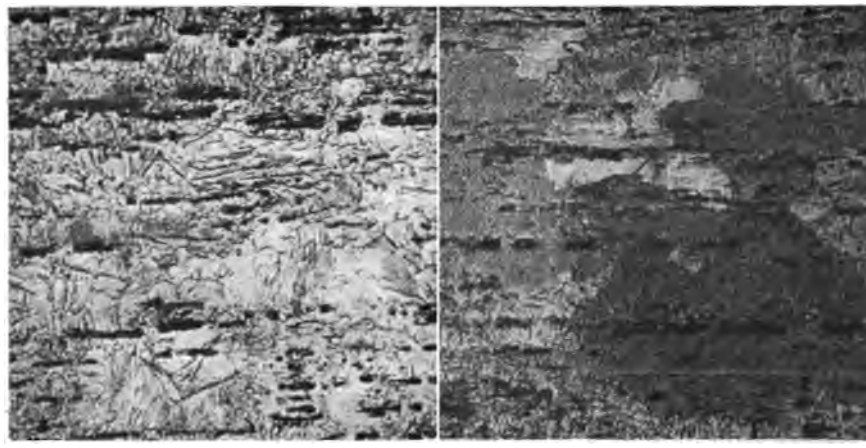
F. Typical of all anneals at 225° C. × 250.

Plate IV.—Unannealed and annealed hard-rolled strip zinc. Samples etched with an aqueous solution of chromic acid and sodium sulfate.



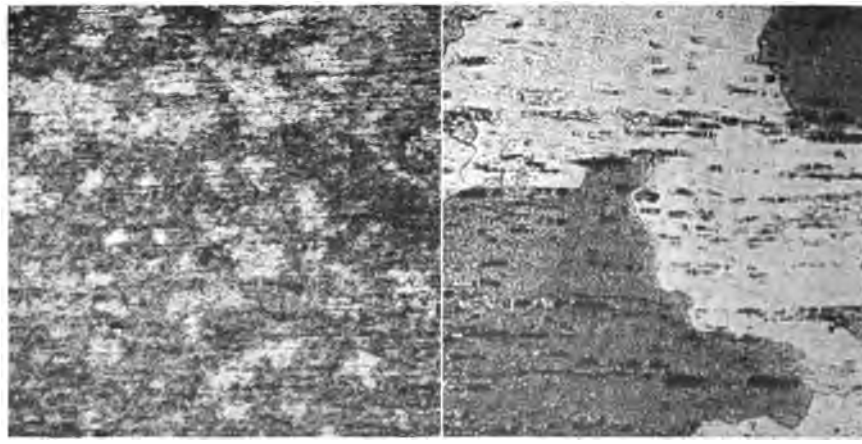
A. × 250. *B.* × 100.

REPRESENTATIVE OF 5-MIN., 30-MIN., 1-HR., AND 5-HR. ANNEALS AT 300° C.



C. TYPICAL OF UNANNEALED STOCK; ALL ANNEALS AT 50 AND 75° C.; AND 5-MIN. OR 30-MIN. ANNEALS AT 100° C. × 250.

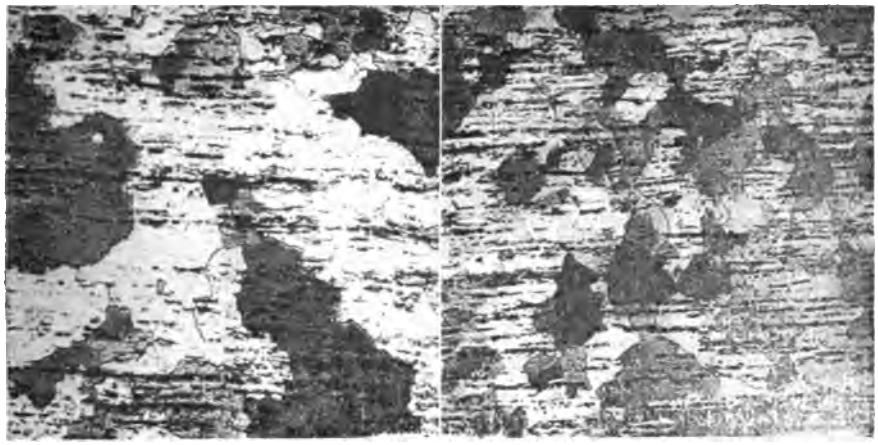
D. TYPICAL OF 1-HR. AND 5-HR. ANNEALS AT 100° C. × 250.



E. STRUCTURE REPRESENTED BY *D*, BUT AT LOWER MAGNIFICATION. × 20.

F. TYPICAL OF ALL ANNEALS AT 125° C. × 250.

PLATE V.—*A* AND *B* REPRESENT HARD-ROLLED STRIP ZINC; *C*, *D*, *E* AND *F*, MEDIUM HARD-ROLLED STRIP ZINC. SAMPLES ETCHED WITH AN AQUEOUS SOLUTION OF CHROMIC

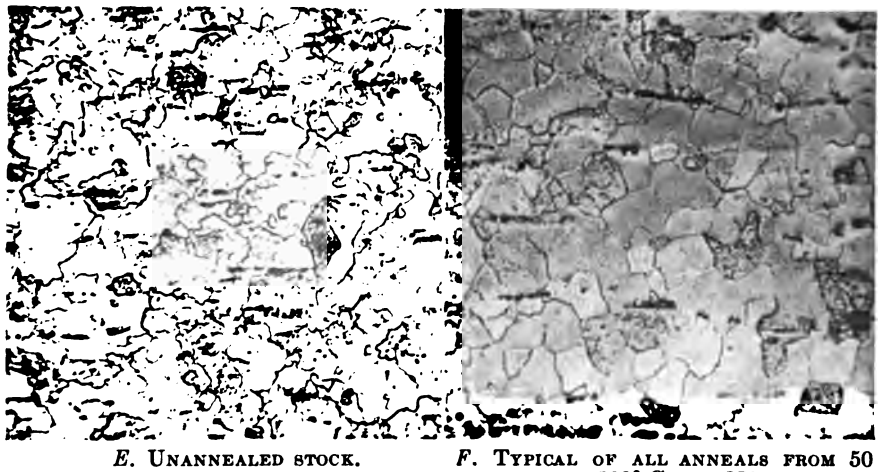


A. Typical of all anneals at 125° C. × 100.

B. Typical of all anneals at 225° C. × 100.

C. Unannealed stock. × 250.

D. Typical of all anneals from 50 to 300° C. × 250.



E. Unannealed stock.

F. Typical of all anneals from 50 to 300° C. × 250.

Plate VI.—*A* and *B* represent medium hard-rolled strip zinc; *C* and *D*, soft-rolled strip zinc; *E* and *F*, dead soft-rolled strip zinc (Horse Head quality). Etched with aqueous solution of chromic acid and sodium sulf

constitutes a certain source of weakness and is largely responsible for the superiority of the Horse Head strip product.

It may be well at this point to state that our tests and direct observations have been made principally on the so-called strip product. There is another form of rolling, called pack-rolling,[18] which offers a better opportunity for an even distribution of the impurities present in common grades of spelter. We have made numerous examinations of pack-rolled sheet and have observed much variation in the quantity and distribution of the fiber. It may be said that the fiber characteristics of metal of Horse Head purity after rolling to a long strip without crosswise rolling at the finish are certainly not inferior to those of pack-rolled zinc of ordinary purity.

In pack-rolling, the finishing gage of the various sheets composing a pack is more or less out of control and rigid requirements in this respect are difficult to meet. No such difficulty is experienced in strip rolling.

Thus, strip-rolling of a sufficiently pure grade of zinc appears to offer the advantage of producing a long strip of metal true to gage and substantially equiaxed in its structural characteristics.

In order to illustrate the important process of grain refining by strain and spontaneous anneal during the rolling process, a partial summary of rolling data with correlated tensile data and micrographs has been prepared. The numerical values are given in Table 7 and the micrographs in Plates II and III. The appearance of the fractured surfaces of the test pieces is fairly well indicated in Fig. 6.

With the aid of this illustrative material, the principal features of the process may be made clear in a few words.

Fig. *A* of Plate II represents the structure of the cast slab. After rolling to a total reduction in thickness of some 50 per cent. the coarse casting grain has become gradually refined through the stages represented by Figs. *B*, *C* and *D* of this plate and also *B*, *C* and *D* of Fig. 6; so as to yield a structure which corresponds to a very satisfactory condition of strength and ductility (compare Table 7). The fracture at this point, as shown at *E*, Fig. 6, indicates uniformity of grain and it is at this stage that the longitudinal samples first stretch and contract after the manner of highly ductile material (see Table 7). The microstructure of slab *E* is not shown, but from *E* to *G*, the latter represented by Fig. *E* of Plate II,

[18] In pack rolling the slabs are first broken down or roughed by rolling each slab singly and always in the same direction down to a thickness of, say, 0.1 in. It is then cut cross wise into a number of pieces which are made into a pack and rolled together through a large number of passes, all at right angles to the previous direction of rolling (roughing) until the required gage is reached. During rolling the pack is split and rearranged a number of times owing to more rapid elongation of the top and bottom sheets. The number of sheets in a pack depends upon their original dimensions and the gage desired at the finish.

there is little change in grain size, while such change in mechanical properties as occurs is probably due to the decreasing thickness of the test piece. It may be pointed out in this connection that samples from slab *F* (0.385 in. thick) when milled down to the thickness of slab *K* (0.057 in. thick) gave substantially the same average value of tensile strength as before but only about half the original ductility. Thus, without accurate knowledge of the relation between thickness and ductility, grain size and ductility cannot be properly correlated in this set of tests.

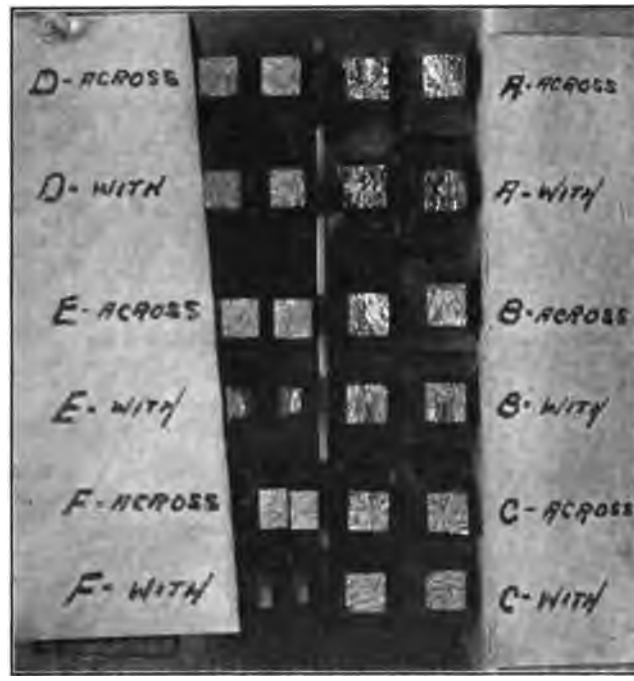


FIG. 6.—ASSEMBLY OF BROKEN TEST PIECES TO INDICATE PROGRESS OF GRAIN REFINING IN ZINC AS ROLLING PROCEEDS FROM ONE STAGE TO ANOTHER. "WITH" INDICATES A TEST PIECE CUT PARALLEL TO DIRECTION OF ROLLING AND "ACROSS" A SPECIMEN CUT AT RIGHT ANGLES TO DIRECTION OF ROLLING.

The average diameter of the grain shown in Fig. *E* of Plate II (slab *G*) is approximately 0.04 mm.

From *G* to *K* (Table 7) the rolling was calculated to produce a harder temper. This is indicated after the first stage (*G* to *H*) by the appearance of strain-hardening in the grain structure as shown in Fig. *F*. The stage from *I* to *J* was marked by non-uniformity. Some parts of the metal are hard, as represented by Fig. *A* of Plate III and other parts are soft, according to Fig. *B* of the same plate. The structure of slab *K* indicates very hard metal (Fig. *C*).

representative of the various types of microstructures developed on annealing the four kinds or "tempers" of strip zinc under consideration.

As a knowledge of the microstructures of these various products is essential to a clear and proper understanding of the results of the mechanical tests we think it advisable to begin with a description of the changes which are effected in the internal structure of the metal by annealing.

First of all, the preparative technique may be briefly described as follows: The rolled surface of the zinc strip is sufficiently smooth to render the usual rough polishing stages of preparation on files and emery papers quite unnecessary. The specimen is polished on each of four disks rotating horizontally at fairly slow speeds. The first two disks are covered with canvas, the third with broadcloth, and the fourth with a jeweler's polishing cloth known as "Syvette." The following grades of emery powder, named in the order in which they are used, serve as the abrasive material, SFX, SF3X, SF10X.[14] The material used on the fourth wheel is a very fine grade of emery powder, prepared by elutriating SF10X emery, previously ground for several weeks in a ball mill. The first three abrasives are applied to the disks in the form of a thin mud while the last abrasive in the form of a heavy suspension is sprayed on the disks from an atomizer. In all of the polishing steps the disks are kept well wet with water and the abrasive material is used sparingly. It is important to note that care should be taken at all times to avoid excessive pressures in handling a specimen on the polishing disks.

After cleaning and drying, the polished specimen is etched from 12 to 20 sec. in a solution made up as follows: 10 gm. c.p. chromic acid (CrO_3), 1.5 gm. c.p. sodium sulfate (anhydrous), 100 c.c. water. This etching solution was developed after considerable experimentation and we have found that it etches most types of rolled or cast zinc satisfactorily.

One characteristic of most of the photomicrographs obtained from rolled strip zinc is the presence of rather unsightly bands whose dimensions and frequency are directly dependent upon the lead content of the metal. Thus it may be seen by referring to the micrographs assembled in these plates that the bands are much less prominent in the Horse Head metal than in metal rolled from common spelter. These bands may be easily developed, apart from any of the other structural characteristics, by means of a momentary dip in concentrated nitric acid. They have nothing to do with the surface marks made on the metal by the rolls but represent a type of fiber due to local concentrations of lead.

However, they give a very exaggerated picture of the lead content

[14] These grades of emery powder can be purchased from the following manufacturers: SFX, Oriental Emery Mills Co., New Haven, Ct.; SF3X and SF10X, Washington Mills Emery Co., North Grafton, Mass.

for two reasons: (1) Local elevations or depressions developed by etching seldom show sharp boundaries but shade off more or less indefinitely into the surrounding material, particularly in the case of soft metals, and under almost any form of illumination produce an exaggerated effect. (2) These bands are not wholly composed of lead but probably originate as follows. Zinc containing a few tenths of a per cent. of lead first freezes pure or substantially pure until the lead content has increased to nearly 1 per cent. This portion of the zinc in the final slab would be free from lead and any consequent bands. During the next stage of freezing, the mother liquor separates not only zinc but at the same time minute droplets[15] of a second solution (96.5 per cent. Pb + 3.5 per cent. Zn) in which all of the lead is concentrated. At the end of this stage the slab will be rigid and it is this combination of zinc and lead which later rolls out into bands. The third and fourth stages of freezing occur within the little droplets of the lead-rich solution, and of course do not influence its position in the slab since this has already been fixed.

Figs. *A* to *F*, Plate IV, and Figs. *A* and *B*, Plate V, illustrate the types of structures existing in unannealed and annealed hard-rolled strip. Fig. *A* of Plate IV shows a severely worked type of structure typical of unannealed hard-rolled strip as well as of the same material annealed for the various periods of time previously mentioned at temperatures of 50 or 75° C., viz., this treatment produces no appreciable change of structure or properties.

On annealing hard-rolled strip for 5 min. at a temperature of 100° C., the structure represented by Fig. *B* is developed. It shows a few large recrystallized grains in a matrix of material of the worked type similar to that shown in Fig. *A*. The phenomena of grain growth are clearly illustrated in Figs. *B*, *C* and *D*. At an annealing temperature of 100° C., grains will apparently start to grow in hard-rolled strip from comparatively few centers. On annealing for longer periods at the same temperature, these grains continue to grow at the expense of the extremely fine-grained hard-worked material and perhaps some smaller recrystallized grains. The growth continues until finally the boundaries of the large growing grains meet, and although grain growth does not entirely cease, this stage marks the cessation of rapid growth of the type in question. Further growth of grain will be accomplished through an absorption of the smaller and weaker grains by the larger and stronger grains; a comparatively slow process at the temperature of 100° C. in strip of this type. This latter statement is borne out by the fact that after an anneal of 30 min. the type of structure shown in Figs. *C* and *D*

[15] The little droplets, while usually scattered, frequently concentrate in small areas of zinc and later these regions roll out into bands of intimately mixed lead and zinc.

is developed and continued annealing for 1 hr. or 5 hr. does not materially increase the grain size.

At higher annealing temperatures, recrystallization starts from a greater number of centers and we have a resulting structure showing more numerous grains of smaller size. The development of structures revealing decreased grain size at the higher annealing temperatures holds true for hard-rolled zinc strip up to the highest temperatures used in our annealing experiments, *i.e.*, a maximum of 300° C. This is illustrated by Figs. *E* and *F*, Plate IV, and Figs. *A* and *B*, Plate V.

The phenomena just described are quite in line with Jeffries'[16] principal generalizations dealing with selective growth. Thus, the coarsest grains are found at an early temperature of recrystallization or in the equiaxing range, and when the equiaxing range is passed rapidly, as must be the case when the samples are dipped directly into an oil bath at a high temperature, smaller grains are formed. Note particularly the small grains of Fig. *B*, Plate V (anneal at 300° C.) as compared with the large grains of Fig. *D*, Plate IV (anneal at 100° C.). We desire particularly to emphasize the fact that the grain-growth characteristics obtained in annealing this thin sheet are of the selective type. This may be partly due to the thinness of the sheet[17] but it is doubtless, to a certain extent, specific with zinc. The graphical aspect of this situation is well illustrated in the ductility curves, for example, Fig. 9, which show a drop to minimum ductility corresponding with maximum grain size in the equiaxing range.

Turning next to the microstructures of the unannealed and annealed medium hard-rolled zinc strip, as illustrated by Figs. *C*, *D*, *E*, and *F*, Plate V, and Figs. *A* and *B*, Plate VI, Fig. *C* shows a type of worked structure representative of the unannealed material and of strip annealed for the four periods at 50° and 75° C., also for the 5- and 30-min. periods at 100° C. Apparently no change in structure has taken place during the above annealing treatment. However, after the 1-hr. and 5-hr. anneals at 100° C. we find that grains have started to grow selectively as shown in Figs. *D* and *E*, Plate V. The growing grains, scattered about in a matrix of fine-grained strain-hardened material, can be seen clearly as bright patches in Fig. *E*, Plate V, taken at a magnification of ×20. The development of this type of structure has already been dealt with under the description of the structures of annealed hard-rolled strip and will not be discussed again. However, in this connection, it is important to note that the less severely strain-hardened material, *i.e.*, medium rolled strip, showed no selective growth when annealed at 100° C. until exposed for 1

[16] Discussion of this subject is in *Trans.* (1916) **54**, 658, and succeeding volumes.
[17] Compare Jeffries (*Trans.* **56**, 575) in this connection.

hr.; while the severely strain hardened, *i.e.*, hard-rolled strip, showed selective grain growth after a 5-min. anneal at this temperature.

An anneal for a period of 5 min. at a temperature of 125° C. developed the coarse-grained structure shown in Fig. *F*, Plate V, and Fig. *A*, Plate VI. Complete recrystallization has taken place with the grains growing selectively and completing their stage of rapid growth within 5 min. Further annealing for periods of 30 min., 1 hr. and 5 hr. brought about no appreciable growth of grain.

As in the case of hard-rolled strip, anneals of medium-rolled strip at the higher temperatures up to 300° C. result in decreased grain size. Fig. *B*, Plate VI, illustrates the structure obtained after annealing at a temperature of 225° C. The decrease in grain size is clearly evident when Figs. *A* and *B*, Plate VI, are compared. In the case of medium hard-rolled strip, however, the grain size produced by an anneal at 300° C. is not as small as would be the case with hard-rolled strip annealed at the same temperature. The reason for this doubtless lies in the fact that at a given high temperature recrystallization starts from a greater number of centers in the case of the severely strain-hardened strip.

Soft-rolled and dead soft-rolled (Horse Head quality) strip zinc are so nearly alike structurally and so similar in their behavior on annealing that they will be described together. Fig. *C*, Plate VI, shows the equiaxed structure of unannealed soft rolled, zinc strip and Fig. *D*, Plate VI, the structure after an anneal at 300° C. The latter micrograph is representative also of all anneals from 50 to 300° C. Fig. *E*, Plate VI, illustrates the typical equiaxed structure of unannealed, dead soft-rolled (Horse Head quality) zinc strip; while Fig. *F*, Plate VI, shows its structure after anneal at 300° C. and this is typical also of all anneals from 50 to 300° C. As can be seen from the micrographs (Figs. *D* and *F*, Plate VI) the only change which has taken place in the structure of either of these kinds of zinc strip on annealing has been an absorption of the very smallest grains by the neighboring larger grains. A development of very large grains does not occur in either of these varieties of strip doubtless because both are already in the equiaxed condition with grains of very nearly equal size, and under such circumstances grain growth appears to be a very slow process—virtually inoperative within the range of annealing periods and temperatures used in our experiments. The grains shown in Figs. *C* and *E*, Plate VI, average approximately 0.02 mm. in diameter and it is important to note that zinc strip having this grain size has been found in practice to be most suitable for drawing operations and press work in general.

The mechanical properties of the various kinds of zinc strip before and after annealing are summarized in Tables 8, 9 and 10. The usual methods were followed in obtaining most of the data contained in the

TABLE 8.—*Scleroscopic Hardness of Unannealed and Annealed Hard-rolled, Medium Hard-rolled, Soft-rolled and Dead Soft-rolled (Horse Head Quality) Zinc Strip*

Annealing Temperature, Degrees C.	Annealing Period	Scleroscopic Hardness			
		Hard-rolled	Medium Hard-rolled	Soft-rolled	Dead Soft-rolled (Horse Head Quality)
Unannealed		29.0	24.0	15.5	15.0
	5 min.	28.0	24.5	15.5	15.0
50	30 min.	28.0	25.0	15.5	15.0
	1 hr.	28.0	25.0	15.5	15.0
	5 hr.	28.0	25.0	15.0	15.0
	5 min.	29.0	25.0	15.0	15.0
75	30 min.	27.5	24.0	15.0	15.0
	1 hr.	24.0	23.5	16.0	15.0
	5 hr.	18.5	24.0	15.0	15.0
	5 min.	19.0	23.5	15.5	15.0
100	30 min.	15.0	20.0	15.5	15.0
	1 hr.	15.0	19.0	15.0	15.0
	5 hr.	15.0	18.0	15.0	15.0
	5 min.	14.5	13.0	16.0	15.0
125	30 min.	15.0	13.0	16.0	15.0
	1 hr.	15.0	13.5	15.0	14.5
	5 hr.	15.0	12.5	15.5	14.0
	5 min.	15.0	14.0	16.5	14.5
150	30 min.	15.0	13.0	15.0	14.0
	1 hr.	15.0	13.5	15.0	14.0
	5 hr.	15.0	13.5	15.0	13.5
	5 min.	15.0	14.0	15.0	13.5
225	30 min.	15.0	13.5	15.0	13.5
	1 hr.	14.0	13.0	14.5	13.5
	5 hr.	15.0	13.0	14.0	13.5
	5 min.	15.0	13.5	15.0	13.5
300	30 min.	15.0	13.5	14.5	13.0
	1 hr.	15.0	13.5	15.0	13.5
	5 hr.	15.0	13.0	13.0	13.5

tables. Only the cold-bending tests require special description. The method of making these tests is briefly described as follows. A test specimen 1 by 1½ in. is cut from the strip in such manner that the grain direction in the strip is either parallel or at right angles to the long dimension of the test piece. The test is made by bending the test specimen at the middle back and forth about an axis parallel to the short dimension

of the specimen. If the grain direction is at right angles to the axis of bending the bend is said to be "across" the grain, while if the reverse is true the bend is "with" the grain. A bend through 180° is counted as

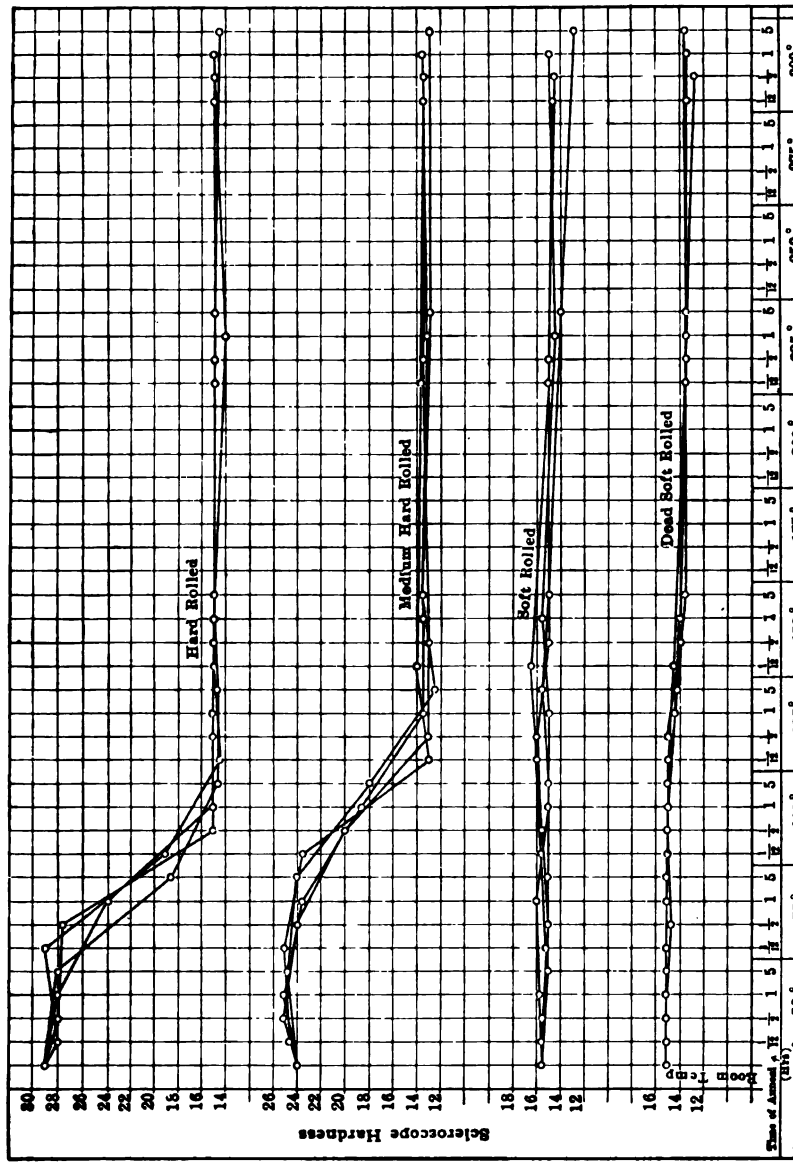


FIG. 7.—SCLEROSCOPIC HARDNESS OF VARIOUS KINDS OF ZINC STRIP (0.010 IN.) BEFORE AND AFTER ANNEALING.

one full bend, a return bend back through 180° a second full bend, and so on. The results are reported as the number of 180° bends necessary to produce the first sign of failure in the strip along the line of bending.

TABLE 9.—*Cold Bend Values of Unannealed and Annealed Hard-rolled, Medium Hard-rolled, Soft-rolled and Dead Soft-rolled (Horse Head Quality) Zinc Strip*

Annealing Temperature, Degrees C.	Annealing Period	Number of Cold Bends							
		Hard-rolled		Medium		Soft-rolled		Dead Soft-rolled (Horse Head Qual.)	
		Across Grain	With Grain	Across Grain	With Grain	Across Grain	With Grain	Across Grain	With Grain
Unannealed		1.5	0.5	4.0	1.0	9.0	4.5	19.5	9.5
	5 min.	1.5	0.5	4.0	1.0	10.5	5.5	19.5	10.0
50	30 min.	1.5	0.5	4.5	1.5	11.0	5.0	21.5	11.5
	1 hr.	1.5	0.5	4.5	1.5	12.5	6.5	19.5	9.5
	5 hr.	1.5	0.5	4.0	1.0	9.5	5.5	19.5	10.5
	5 min.	1.5	0.5	3.5	1.0	11.5	5.5	23.5	11.5
75	30 min.	1.0	0.5	4.0	1.0	12.5	5.5	21.5	11.5
	1 hr.	0.5	0.5	4.5	1.0	11.0	6.5	22.5	10.5
	5 hr.	0.5	0.5	3.5	1.0	12.5	7.0	22.5	11.5
	5 min.	2.5	1.0	4.0	1.0	11.5	8.5	22.5	13.5
100	30 min.	7.5	1.5	3.5	1.0	10.5	6.5	24.5	12.5
	1 hr.	7.5	2.0	3.5	0.5	11.0	5.5	19.5	11.5
	5 hr.	7.5	1.5	4.5	1.0	11.5	5.5	21.5	12.5
	5 min.	10.5	2.0	5.5	1.5	7.5	4.5	21.5	11.5
125	30 min.	10.5	3.0	5.5	1.5	10.5	5.5	22.5	12.5
	1 hr.	10.5	3.0	5.5	1.5	10.5	5.5	22.5	12.5
	5 hr.	11.5	1.5	5.5	1.5	10.5	6.5	22.5	12.5
	5 min.	13.5	4.0	7.5	3.0	12.0	11.5	25.5	14.0
150	30 min.	15.0	5.0	9.5	3.5	12.0	6.5	25.5	14.5
	1 hr.	14.0	4.0	9.5	5.5	10.5	5.0	25.5	14.5
	5 hr.	13.5	4.5	9.5	3.0	10.5	5.5	26.0	15.0
	5 min.	21.5	7.5	13.5	5.5	8.5	7.5	25.5	15.5
225	30 min.	21.5	7.5	14.5	5.5	7.5	7.5	25.5	15.5
	1 hr.	21.5	7.5	15.0	5.5	8.0	7.5	25.5	15.5
	5 hr.	21.5	7.5	13.5	5.5	13.5	7.5	25.5	15.5
	5 min.	14.5	5.5	15.5	5.0	9.5	5.5	28.0	16.0
300	30 min.	19.5	5.5	15.5	5.5	9.5	5.0	27.5	11.5
	1 hr.	18.5	5.5	13.5	3.5	9.5	5.5	26.5	9.5
	5 hr.	10.5	4.0	8.0	1.5	7.5	4.5	11.5	5.5

The results included in the tables of data are illustrated graphically in Figs. 7, 8 and 9.

The curves of Fig. 7 show very clearly the effect of annealing on the scleroscopic hardness of strip zinc. In the case of hard-rolled strip,

marked softening occurs even after the brief anneals at 75° C. while complete softening takes place after a 1-hr. anneal at 100° C. and is coincident

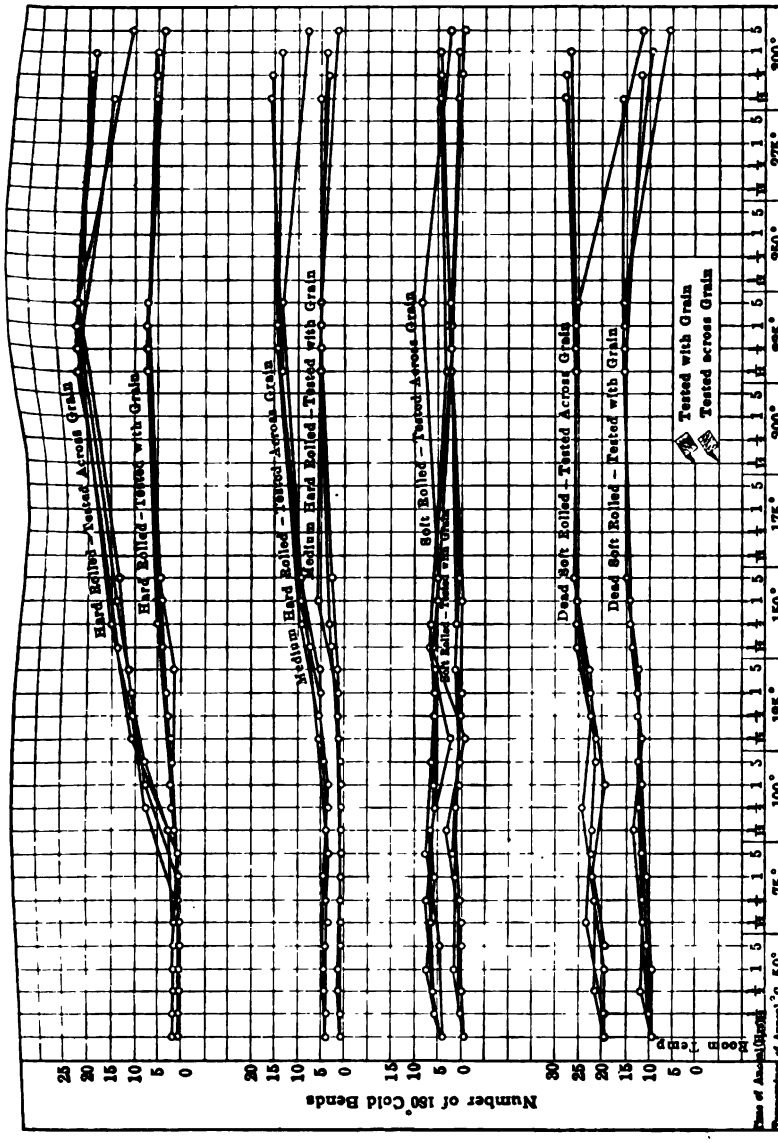


FIG. 8.—COLD-BENDING VALUES OF VARIOUS KINDS OF STRIP ZINC (0.010 IN.) BEFORE AND AFTER ANNEALING.

with complete recrystallization (see Figs. *C* and *D*, Plate IV). Annealing at higher temperatures does not further soften the material.

Medium hard-rolled strip does not begin to show a drop in hardness until an annealing temperature of 100° C. has been reached. It is at

TABLE 10.—*Ductility (Olsen Cupping Tests) of Unannealed and Annealed Hard-rolled, Medium Hard-rolled, Soft-rolled, and Dead Soft-rolled (Horse Head Quality) Zinc Strip*

Annealing Temperature, Degrees C.	Annealing Period	Ductility (Height of Cup, in Inches)			
		Hard-rolled	Medium Hard-rolled	Soft-rolled	Dead Soft-rolled (Horse Head Quality)
Unannealed		0.443	0.354	0.328	0.378
50	5 min.	0.447	0.353	0.340	0.367
	30 min.	0.429	0.332	0.312	0.361
	1 hr.	0.432	0.363	0.323	0.374
	5 hr.	0.377	0.364	0.306	0.367
75	5 min.	0.426	0.341	0.330	0.378
	30 min.	0.352	0.313	0.313	0.360
	1 hr.	0.237	0.342	0.306	0.340
	5 hr.	0.219	0.304	0.301	0.344
100	5 min.	0.262	0.258	0.309	0.381
	30 min.	0.233	0.238	0.314	0.376
	1 hr.	0.188	0.225	0.301	0.365
	5 hr.	0.184	0.222	0.308	0.363
125	5 min.	0.259	0.253	0.311	0.372
	30 min.	0.242	0.237	0.310	0.383
	1 hr.	0.249	0.249	0.313	0.340
	5 hr.	0.204	0.214	0.296	0.334
150	5 min.	0.275	0.265	0.291	0.358
	30 min.	0.275	0.263	0.301	0.351
	1 hr.	0.274	0.234	0.294	0.334
	5 hr.	0.264	0.251	0.296	0.339
225	5 min.	0.296	0.307	0.310	0.358
	30 min.	0.291	0.305	0.311	0.351
	1 hr.	0.296	0.298	0.311	0.334
	5 hr.	0.293	0.284	0.310	0.339
300	5 min.	0.292	0.278	0.300	0.349
	30 min.	0.278	0.309	0.304	0.340
	1 hr.	0.263	0.289	0.291	0.333
	5 hr.	0.225	0.252	0.259	0.300

this temperature that recrystallization is first noticeable, Figs. *D* and *E*, Plate V. Complete softening is reached on annealing at a temperature of 125° C., which is also the temperature at which we find complete recrystallization (see Fig. *F*, Plate V, and Fig. *A*, Plate VI).

The hardness of soft-rolled and dead soft-rolled (Horse Head quality)

zinc strip shows a very slight drop on annealing. The microstructures before and after annealing in these cases would lead one to expect no great change of properties.

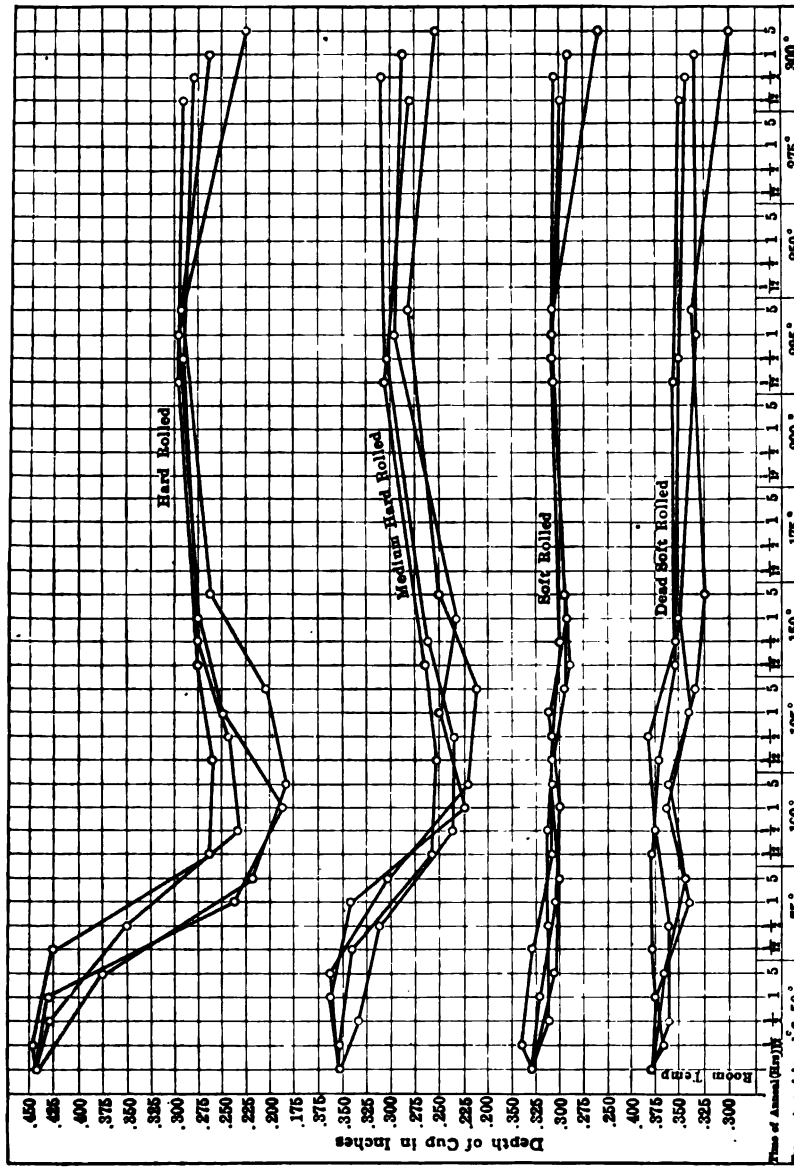


FIG. 9.—DUCTILITY (OLSEN CUPPING MACHINE) OF VARIOUS KINDS OF STRIP ZINC (0.010 IN.) BEFORE AND AFTER ANNEALING.

The effect of annealing on the cold-bending properties of the four kinds of zinc strip is shown graphically in Fig. 8. In general, annealing may be said to improve the bending qualities of the unannealed strip.

This improvement is most noticeable in the case of the hard-rolled and medium hard-rolled strip but is also apparent to some extent with the soft-rolled and dead soft-rolled (Horse Head quality) strip. The improvement in the bending qualities seems to be greatest where the direction of bending is across the grain.

The effect of annealing on the ductility, as measured by the Olsen cupping machine, is brought out clearly by the curves shown in Fig. 9. Hard-rolled strip shows a decrease in ductility after anneals at 75° and 100° C., reaching its lowest point after the longer anneals at the latter temperature. The photomicrographs of this material (Figs. *C* and *D*, Plate IV) show the coarsest grain after anneal at 100° C. As the grain size decreases in the upper temperature range of anneal (see Figs. *E* and *F*, Plate IV, and Figs. *A* and *B*, Plate V), we observe an increase in the ductility over its low value at 100° C.

Somewhat similar effects are observed in the case of medium hard-rolled strip, except that the drop and subsequent rise in the ductility curve are not as marked as in the case of hard-rolled strip. The ductilities of soft-rolled and dead soft-rolled (Horse Head quality) strip are not changed materially on annealing for the reason already advanced to explain the hardness results.

In order to save space and effort we think it inadvisable to include data from tensile tests on the four kinds of thin annealed strip. Briefly, the indications of the tensile tests are as follows: Hard-rolled strip suffers a sharp drop in tensile strength on annealing as the coarsening sets in, viz., at 100° to 125° C. The tensile strength in tests made across the grain may fall as low as 20,000 lb. per sq. in. from an average initial value of 40,000 lb. per sq. in. and as low as 16,000 lb. per sq. in. in tests with the grain, from an initial value of 35,000 lb. per sq. in. It rises, subsequently, in the case of annealing at higher temperatures, owing to the change in grain characteristics previously pointed out. The percentage elongation in 2 in. also decreases on annealing, but not as noticeably. Annealed values may be as low as 30 with a subsequent rise usually carrying it up to the initial value of some 40.

In the case of soft-rolled and dead soft-rolled (Horse Head quality) material, the change in tensile properties on annealing may be characterized as inappreciable provided the material has not been locally strained before annealing. In the latter event, the results after annealing are likely to be erratic.

The practical application of the information brought out in this section of the paper will be evident when the results are considered in detail with respect to any given service requirement. We think it unnecessary to discuss this subject in general terms.

5. Dynamic Ductilities

We find that most customers who use zinc for drawing purposes base their determination of its fitness for such work very largely upon scleroscopic hardness tests in connection with certain simple indications ascertained by ordinary handling and inspection of the material (its feeling of stiffness, rough bending properties, etc.).

There is no doubt as to the general value of the indications of the scleroscope, but the softness which it indicates may appear as an entirely misleading factor in judging the drawing qualities of the metal; for

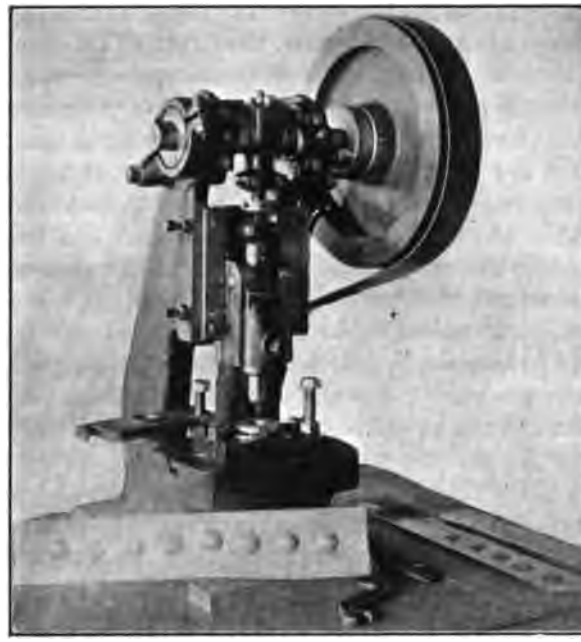


Fig. 10.—Modified Bliss press used in making dynamic ductility tests.

example, in the case of metal annealed so as to produce a coarse grain. The ordinary Erichsen or Olsen cups also give misleading indications when taken by themselves; for an extremely hard-rolled strip is likely to give a deeper cup than soft-rolled metal of the very best drawing quality in practice.

We have lately come to the conclusion that the only means of obtaining reliable practical indications of the drawing quality of a material is to deform the metal at a rate comparable with that which obtains in practice in actual press work. In this connection, we have found it desirable to use a plunger and die virtually identical with those built into the Olsen ductility machine, but operated so as to draw the cup rapidly. Tests were carried out on several types of experimental appa-

ratus operating on the principle of the Charpy impact testing machine. In the course of our experiments along this line, tests were made on a small Bliss press adapted to take the necessary cupping tools, etc. We found that this method of making dynamic ductility tests was superior to the other methods tried for several reasons, among which were ease of operation, and control of cupping speed.

This machine is illustrated in Fig. 10, which shows the plunger, die, and clamp for holding the material tight to the face of the die while the cup is being made, thus duplicating the conditions under which a strip is clamped and tested in the Olsen ductility machine. The die threads into a steel plate bolted to the bed of the machine and by screwing it up and down any depth of cup within the limits of the machine can be made, since the travel of the plunger remains constant. The outer edge of the top of the die is graduated and the stroke of the plunger adjusted so that as the die is screwed up or down the depth of cup thus determined can be measured to 0.001 in. By means of a system of gears and various sized pulleys, the press may be made to operate at quite widely varying speeds, *i.e.*, from 13 to 102 strokes per minute. When the press is in operation, the flywheel will be turning at the predetermined speed, but by means of a tripping device the plunger is permitted to make only one stroke whenever it is desired to form a cup.

The testing procedure is briefly described as follows. The die is first set to produce a cup the depth of which represents an estimate of the probable dynamic cupping value of the strip. One end of the strip is placed over the die and the strip is held down tight against the flat die face by means of the clamp shown. The press is operated at a selected speed and the cup made in one stroke of the plunger. If the cup shows no break the die is set for a slightly deeper cup and this second cup is made in a nearby region of the test strip. This procedure is continued until a fractured cup results. If, however, fracture should occur in the first trial cup, a reverse procedure would be employed according to which a series of cups would be made with the die set to give decreasing depths of cup. Thus, by a series of tests the depth of cup is found at which fracture just takes place. Several cups made at depths slightly above and below this point will fix its location accurately. The dynamic ductility value is taken as the depth of cup in thousandths of an inch, which if increased by a few thousandths will produce a fracture. The end point in this method of testing is as clearly marked as in ductility tests on the ordinary Olsen cupping machine. Repeated trials with duplicate test strips will give end points checking the original within 0.005 to 0.010 in.

After the various details connected with the development of this testing method were worked out, we studied the effect of the rate of cupping on the depth of cup obtained. These experiments were conducted at speeds ranging from 0.34 to 163 in. per. min. Speed is defined in this

connection as the average rate of cupping in inches per minute. The slowest speeds were obtained by using the ordinary Olsen cupping machine. The intermediate and highest speeds, varying from 3 to 163 in. per. min., were obtained by adjusting the drive connected with the Bliss press.

Before combining the data from the two different forms of apparatus we made a direct comparison between the two machines operating at a very slow speed, viz., by actuating the Bliss press carefully by hand to give two strokes per minute, which is equivalent to an actual average drawing speed of 3 in. per min., and by turning the wheel of the Olsen cupping machine at a rate of 128 r.p.m., which is also equivalent to this cupping speed. The tests made on the two machines at the above speed gave cups whose depths agreed within some 15 per cent. While we would like to see a closer agreement between the results in question, it must be remembered that it is difficult to operate the Olsen machine at anything approaching the speed used in the comparison tests without over running the break and it is equally difficult to operate the press smoothly at any Olsen speed. It may be mentioned that the motion of the plunger in the two machines is quite different. With the Olsen machine we have uniform motion in a straight line, while in the case of the Bliss press we have simple harmonic motion, with the rate of deformation greatest at the start. The comparisons can therefore be only approximate.

TABLE 11.—*Ductility of Hard-rolled, Medium Hard-rolled, Soft-rolled, and Dead Soft-rolled (Horse Head Quality) Zinc Strip at Different Speeds of Drawing*

Hard-rolled		Medium Hard-rolled		Soft-rolled		Dead Soft-rolled (Horse Head Quality)	
Average Speed of Cupping, Inches per Minute	Depth of Cup, Inch	Average Speed of Cupping, Inches per Minute	Depth of Cup, Inch	Average Speed of Cupping, Inches per Minute	Depth of Cup, Inch	Average Speed of Cupping, Inches per Minute	Depth of Cup, Inch
0.34	0.415	0.34	0.329	0.34	0.283	0.34	0.341
1.30	0.382	1.30	0.290	1.30	0.295	1.30	0.339
2.60	0.338	2.60	0.250	2.60	0.287	2.60	0.338
3.10	0.264	2.85	0.225	3.00	0.250	3.20	0.245
16.90	0.184	18.10	0.210	19.80	0.254	21.10	0.300
62.00	0.154	70.00	0.195	79.00	0.254	85.00	0.300
120.00	0.150	135.00	0.190	154.00	0.250	163.00	0.286

NOTE.—The tests at the three lowest drawing speeds were made on the Olsen cupping machine; all others on the Bliss press.

Table 11 shows the cupping data obtained at indicated average speeds varying from 0.34 to 163 in. per min. The four different kinds of zinc strip which, as we have previously pointed out, just about cover all

ordinary possibilities as to temper, etc., in a rolled zinc product, were all used in these tests. These are designated as (1) hard-rolled, (2) medium

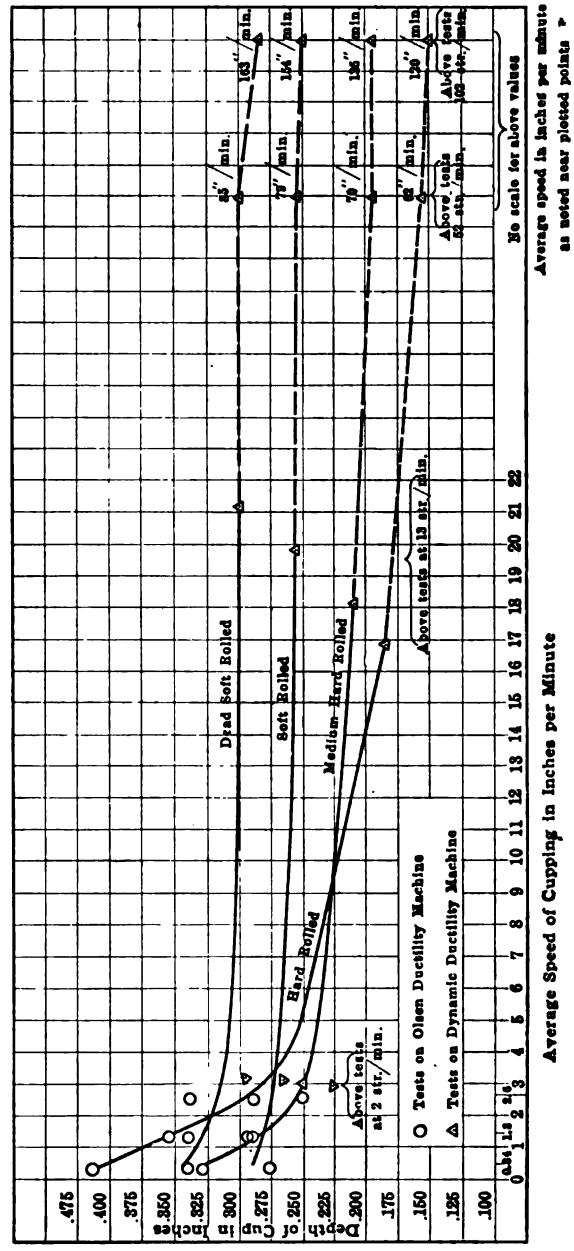


FIG. 11.—DUCTILITIES OF FOUR KINDS OF STRIP ZINC AT DIFFERENT DRAWING SPEEDS.

hard-rolled, (3) soft-rolled and (4) dead soft-rolled (Horse Head quality).

The results appearing in the foregoing table are shown graphically in Fig. 11. The curves indicate clearly the utility of a dynamic ductility test, viz., they indicate why certain kinds of zinc strip are better fitted for drawing work than others. For example, hard-rolled strip tested in the Olsen cupping machine at the speed ordinarily employed in making these tests will show a better cupping value than any other kind of zinc strip. This same material tested dynamically at speeds commensurate with those used in ordinary drawing practice gives values which show beyond question that it is the least adaptable to ordinary drawing requirements of any of the various kinds of zinc tested. The medium hard-rolled material shows somewhat similar characteristics and although its dynamic value is above that of hard-rolled material it is still far from a good drawing zinc. Soft-rolled and dead soft-rolled (Horse Head quality) strip show only slight decreases in ductility when tested at the higher speeds of cupping; quite contrary to what was observed with the two other kinds of zinc. It is important to note that, except in the case of the hard-rolled zinc strip, all of the curves shown in Fig. 11 indicate that after an average cupping speed of approximately 5 in. per min. is reached, there is little variation in the depth of cup with increase in speed up to 163 in. per min.

Dynamic ductility tests were thereupon made on samples of unannealed and annealed hard-rolled, medium hard-rolled, soft-rolled and dead soft-rolled (Horse Head quality) zinc strip. The various kinds of zinc were annealed for 1 hr. at each of the following temperatures; 50°, 75°, 100°, 125°, 150°, 225° and 300° C. These materials were first tested in the Olsen machine, at an ordinary low speed of 0.34 in. per min. We have used the term "static ductility" to characterize the latter tests and the term "dynamic ductility" to characterize the tests made on the Bliss press.

In testing the annealed material on the latter machine, a speed of 50 strokes per minute was selected. This corresponds to an average cupping speed of 60 to 90 in. per min., depending upon the depth of cup, and all of these dynamic ductility tests were made at this one speed.

TABLE 12.—*Static and Dynamic Ductility Tests of Unannealed and Annealed Hard-rolled, Medium Hard-rolled, Soft-rolled and Dead Soft-rolled (Horse Head Quality) Zinc Strip*

Annealing Temperature, Degrees C. Time of Anneal, 1 Hr.	Hard-rolled		Medium Hard-rolled		Soft-rolled		Dead Soft-rolled (Horse Head Qual.)	
	Static Ductility	Dynamic Ductility	Static Ductility	Dynamic Ductility	Static Ductility	Dynamic Ductility	Static Ductility	Dynamic Ductility
Unannealed	0.389	0.190	0.353	0.180	0.277	0.245	0.360	0.275
50	0.411	0.195	0.347	0.195	0.286	0.260	0.358	0.280
75	0.448	0.205	0.323	0.180	0.303	0.265	0.342	0.275
100	0.215	0.100	0.256	0.140	0.329	0.275	0.352	0.280
125	0.162	0.170	0.192	0.160	0.308	0.265	0.365	0.285
150	0.196	0.210	0.217	0.210	0.290	0.255	0.358	0.285
225	0.195	0.165	0.213	0.170	0.274	0.240	0.383	0.305
300	0.186	0.175	0.196	0.175	0.257	0.255	0.377	0.290

The results of the tests are summarized in Table 12, and illustrated graphically in Fig. 12.

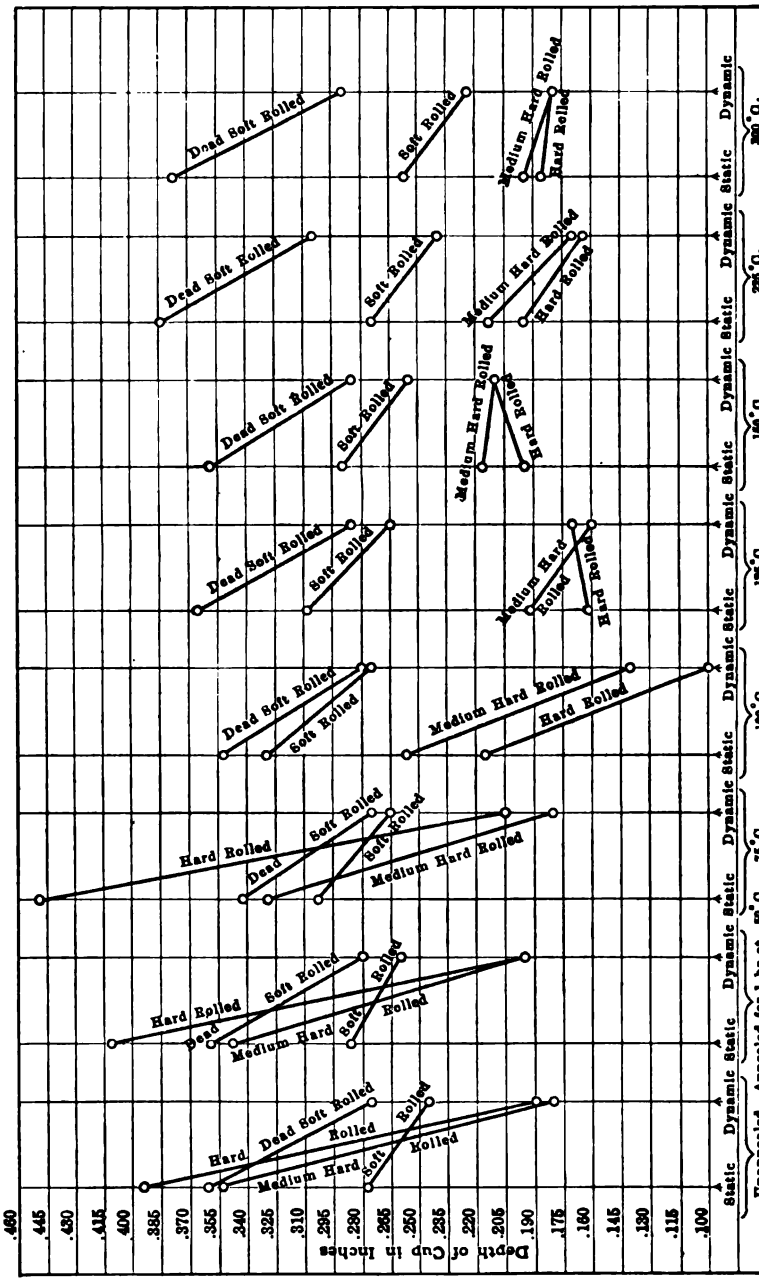


FIG. 12.—STATIC AND DYNAMIC DUCTILITIES OF FOUR KINDS OF STRIP ZINC BOTH UNANNEALED AND ANNEALED.

As may be readily seen from the chart representing these results, in general where there are decreases apparent in the static ductility value of a strip due to the effect of annealing, similar decreases mark the dynamic values. In the case of the dynamic test, however, the percentage decrease is not so great.

Hard-rolled and medium hard-rolled strip show minimum dynamic ductility values after an anneal at a temperature of 100° C. As has been previously brought out, this is the temperature at which these products coarsen most seriously on annealing (see Figs. *C* and *D*, Plate IV, and Figs. *D* and *E*, Plate V). The dynamic ductilities of soft-rolled and dead soft-rolled (Horse Head quality) metal are not changed materially on annealing.

In order that some idea may be had of the drawing properties of strip zinc as compared with those of sheet zinc and strip brass, static and dynamic tests were made on (1) the four kinds of strip zinc, (2) four samples of sheet zinc, representing the product of other mills, and (3) samples of unannealed and annealed 70/30 brass. The samples of sheet zinc, 0.010 in. in thickness, are designated as competitive material No. 1, No. 2, etc. The brass, 0.010 in. thick, as in the case of the other materials, was tested after cold reductions by rolling amounting to 23 and 50 per cent., respectively, and also after annealing the hardest product (15 min.) at each of the following temperatures, 450°, 550°, 650° and 750° C. The static ductility tests were made in the ordinary manner on an Olsen machine at a drawing speed of 0.34 in. per min., while the dynamic tests were made on the Bliss press operating at a speed of 50 strokes per min., corresponding to an average rate of drawing of 60 to 100 in. per min., as previously described.

The results of these tests appear in Table 13 and in Fig. 13.

TABLE 13.—*Static and Dynamic Ductility Tests of Hard-rolled, Medium Hard-rolled, Soft-rolled and Dead Soft-rolled Zinc Strip; Competitive Sheet Zinc; and* 70/30 *Brass Annealed at Various Temperatures*

Strip Zinc (0.010 In.)	Ductilities: Depth of Cup, Inches		Competitive Sheet Zinc (0.010 In.)	Ductilities: Depth of Cup, Inches		70–30 Brass (0.010 In.)	Ductilities: Depth of Cup, Inches	
	Static	Dynamic		Static	Dynamic		Static	Dynamic
Hard-rolled.....	0.415	0.155	C.M.1....	0.291	0.190	Reduced 23 per cent. by rolling	0.248	0.160
Medium-rolled....	0.329	0.195	C.M.2....	0.291	0.195	Reduced 50 per cent. by rolling	0.228	0.165
Soft-rolled.....	0.277	0.255	C.M.3....	0.284	0.205	Annealed ¼ hr. at 450° C.	0.445	0.360
Dead soft-rolled...	0.341	0.300	C.M.4....	0.283	0.210	Annealed ¼ hr. at 550° C.	0.488	0.380
						Annealed ¼ hr. at 650° C.	0.590	0.410
						Annealed ¼ hr. at 750° C.	0.536	0.410

Attention may be directed to several items of interest brought out by these tests. First, with respect to tests made on the various kinds of strip and sheet zinc, it is apparent that dead soft-rolled and soft-rolled strip are better for drawing than any of the competitive sheet samples.[18]

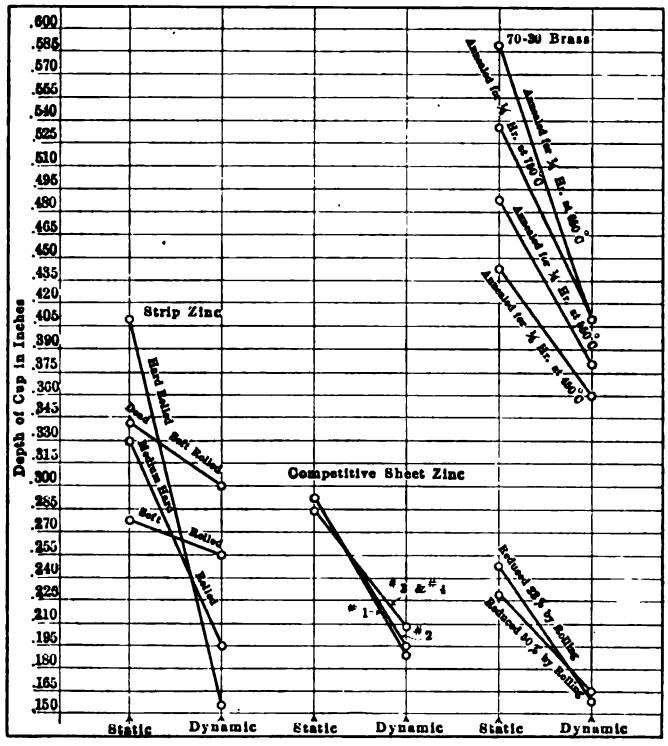


FIG. 13.—STATIC AND DYNAMIC DUCTILITIES OF (1) FOUR KINDS OF STRIP ZINC, (2) COMPETITIVE SHEET ZINC, (3) 70/30 BRASS OF VARIOUS TEMPERS.

Turning next to the static and dynamic ductility tests on brass we find that the same general relationship exists between the two sets of values in the case of brass as in the case of zinc, viz., the static ductility values are uniformly higher than the dynamic ductility values. As may be seen by inspection of the curves, the static and dynamic values for hard brass are lower than the static and dynamic values for either strip or sheet zinc, while the static and dynamic values for annealed brass are considerably higher than the zinc values.

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[18] We feel that it would be unprofessional to give the origin of this material, which, however, was intended to represent some diversity in its particular field. Obviously, we cannot authoritatively report as to the total range of properties covered by sheet zinc, solely on the basis of the material in hand.

We have not gone very extensively into the question of dynamic properties of brass; for example no tests were made after very light reductions. However, from the general nature of the comparisons already available, it would appear that the best drawing values of zinc are substantially equivalent to what might be expected in the case of 70/30 brass after a cold reduction in the neighborhood of 10 per cent.

The static and dynamic ductilities of both 80/20 and 90/10 brass (annealed) appear to lie closer to one another than in the case of 70/30 brass (curves not shown).

It is interesting to note that although the static ductility values of brass annealed at 750 and 450° C. are quite widely separated, the difference is less noticeable in the case of the dynamic ductility values given by the same material.

This would seem to indicate a rather higher drawing value than has usually been ascribed to brass annealed at quite low temperatures. This of course does not take the load factor into consideration, *i.e.*, it undoubtedly requires less energy to produce the cup in coarse-grained than in fine-grained brass and the general depreciation of the drawing equipment would be less under the former conditions.

6. Stiffness of Worked Zinc; Alloyed Products

The early German authors (see Section 1 of this paper) have left a very good picture of the characteristics of impure hard-rolled zinc under tensile loading. It is quite clear from theoretical considerations that material of this sort would under ordinary conditions roll or draw into a stiffer material than very pure zinc. This is fully borne out by such tests as we have seen.

The ordinary conception of stiffness in a metal rod, for example, is gained by handling it, *i.e.*, by observing the resistance which it offers to bending whether it does or does not return to its initial shape after such manipulation.

The simple engineering conception of stiffness deals with the action of stresses within the elastic range and is measured by the slope of the stress-deformation curve below the elastic limit, *i.e.*, it is in effect defined by the modulus of elasticity. In this sense cartridge brass and rolled zinc are about equally stiff, viz., the modulus of elasticity is from 11,000,000 to 11,500,000 in both cases and the condition of the metal as regards temper does not appear to affect this value greatly.

However, in such a comparison no account is taken of the extreme load which the metal will bear and still bend in accordance with the ratio of stress to deformation as expressed in the above modulus. In the case of zinc this is a very low value, and after passing this value the deformation increases rapidly as the load builds up, *i.e.*, the metal bends freely. It is also low in the case of annealed brass, but high in the case

of cold-worked brass. Thus, the latter material is stiff in the full sense that it bends or stretches only slightly with each increment of stress up to very high values of stress.

The stiffness of zinc in this sense may be raised by alloying. Thus, stress-deformation curves 1 and 2 of Fig. 14 represent relatively pure (Horse Head) zinc rod and an alloyed rod containing 1 per cent. of cop-

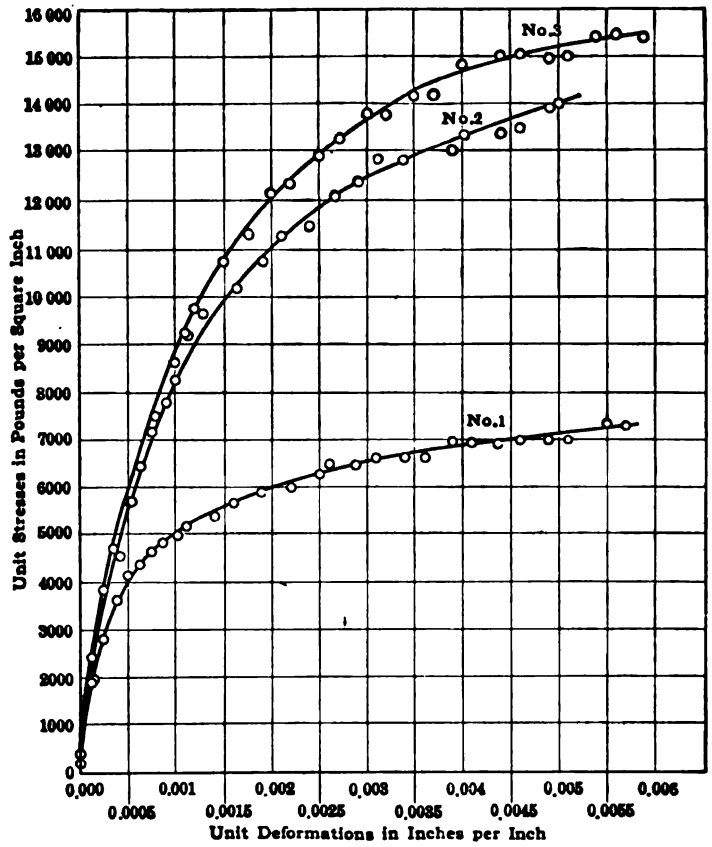

FIG. 14.—STRESS-DEFORMATION CURVES OF PURE AND ALLOYED ZINC ROD. SPEED OF POLLING, 0.052 IN. PER MINUTE.

per, respectively. This material was made by rolling a 2-in. wire bar through grooves of varying section down to a thickness of $\frac{5}{8}$ in. and then drawing as cold as possible to the final diameter of $\frac{1}{4}$ inch.

It is observed that the soft pure zinc reaches high values of deformation at relatively low stresses while the copper alloy requires much higher stresses for similar values of deformation. For example, the latter material requires nearly twice as great a stress as the former to produce a unit deformation of 0.004 in. per in. It should be observed that alloy-

ing of this character does not produce any marked or practically useful increase in the range of true elastic action; it merely makes the material more sluggish in flowing to accommodate the stress.

Viewed in another light, it produces an effect similar to that which would accompany a considerable increase in the rate of loading.

In thus pointing out the true character of these changes we do not desire to minimize their importance. The above change in stress-strain characteristics really constitutes a very useful improvement in stiffness according to the ordinary or more or less free interpretation of this term. Needless to say, it does not signify a type of alteration sufficiently drastic to bring zinc into competition with steel as a material for gun barrels or watch springs.

It is interesting to inquire into the reason for the above changes and first of all some classification of the structural changes produced by alloying seems necessary.

Most authors have used either copper or aluminum, or both, in seeking to improve zinc by alloying. According to the researches of Shepherd,[19] Tafel,[20] and Parravano,[21] solid zinc can retain some 2½ per cent. of the former metal in solution at all temperatures below the freezing point. In the case of aluminum, early researches have indicated a solid solubility of some 3 per cent. in zinc but the very recent authoritative work of Bauer and Vogel[22] places the limit of solubility at ¾ per cent. There are no indications that any other metal dissolves appreciably in solid zinc. Thus, the common method of profoundly altering the properties of a metal by freely dissolving another metal in it (*e.g.*, making copper into the most ductile brass by saturating it with zinc or into the toughest bronze by saturating it with tin) cannot be utilized in the case of zinc. Even the most promising metal, copper, appears to be considerably less soluble in solid zinc than the figures quoted above would indicate; we have been unable to introduce much more than 1½ per cent. of copper into solid solution in zinc.

There is hardly enough copper present in the alloy used in the tests just described (1 per cent.) to alter its mechanical properties to any great extent—1 per cent. of zinc in copper does not greatly modify the metal; it requires some 10 or 20 per cent. to produce a marked change in properties. Hence, the marked difference between the pure zinc and the copper alloy represented in Fig. 14 is probably due solely to the known tendency of impurities even in small amount to raise the softening temperature of the metal and cause it to strain harden more effectively.

If this is true, a little lead and cadmium should produce about the same effect and, as a matter of fact, ¼ in. rod made in the same way from

[19] *Jnl. Phys. Chem.* (1904) **8**, 421.
[20] *Metallurgie* (1908) **5**, 377 et seq.
[21] *Gazz. Chim. Ital.* (1914) **44** (2), 478.
[22] *Loc. cit.*

a common grade of spelter shows about the same stress-deformation characteristics as the copper alloy in question. The ratios of stress to unit deformation at a deformation value of 0.004 in. per in. are 3,500,000 and 3,350,000 respectively.

There is another form of alloying which might be expected to prove efficient in increasing the stiffness of zinc. We refer to that type of alloying which is illustrated by the familiar relationship between soft iron and annealed steel. Here, we have a hardening and stiffening constituent, namely iron carbide, thoroughly distributed in the form of fine plates or granules throughout the matrix of soft iron.

The result is a great increase in the range of stress through which the metal may be bent or stretched without permanent set.

While there appears to be no possibility of developing a structure in zinc analogous to the pearlitic structure of annealed eutectoid steel, there are other possibilities of incorporating a finely divided reinforcing material with zinc so as to simulate the effect produced by cementite in a soft iron matrix.

The stress-deformation characteristics of an alloy of this type which may be commercially worked into rod, wire, etc., are shown in the uppermost curve (No. 3) of Fig. 14. Here we note a further improvement, in respect to stiffness. The values of unit stress which produce a unit deformation of 0.004 in. per in. are 1,725,000; 3,350,000; and 3,700,000 in alloys Nos. 1, 2, and 3, respectively.

7. Successful Applications

Rolled zinc has been known to the public in this country for a number of years. This acquaintance has been only a casual one, having been confined to the use of zinc as a covering for tables and as a protector under or behind stoves. It has also been known as an excellent material for the rubbing part of washboards. In times gone by most of our bath tubs were lined with zinc, but in recent years this usage has entirely disappeared.

Rolled zinc (strip and sheet) has been used extensively in Europe for many years,[22] but only recently has it had a wider application in this country. The uses for this product are quite numerous, and are somewhat surprising to the newly initiated.

The uses for rolled zinc may be classified into four groups:

1. Its adaptation due to its electrical and electrochemical properties.
2. Its adaptation due to its resistance to atmospheric corrosion and its anti-staining features.

[22] The foreign uses of rolled zinc in 1905 are well described in an article: "Manufacture and Uses of Rolled Zinc" emanating from La Soc. de la Vieille-Montagne and published in *L'Industrie du Zinc*, pp. 63–66.

3. Its adaptation to pressed, drawn, or spun articles of manufacture, due to its cheapness in competition with brass, aluminum and copper.

4. Miscellaneous.

A classified list of some successful uses follows:

1. *On Account of Its Electrical and Electrochemical Properties.*—Boiler plates, hull plates, cyanide shavings, primary battery plates, soldered dry battery casings, drawn dry battery casings, replaceable fuses, non-magnetic boxes enclosing electrically operated switches, drawn cases for electrical measuring instruments.

FIG. 15.—DRAWN AND SOLDERED BATTERY CANS.

2. *On Account of Its Permanency and Anti-staining Features.*—Sheet zinc roofs, zinc shingle roofs, hip-rolls, ridge-rolls, valleys, leaders or conductor pipes and gutters, roofing nails, weather stripping, glaziers' points, art glass windows, electrical fittings exposed to the atmosphere, corset eyelets and corset steel tips, washboards, linings for mechanical washing machines, metal tags, shoe polish boxes, shoe and other lacing tips.

3. *Pressed, Drawn or Spun Articles.*—Addressograph plates, jar tops, piano hinges, smokeless powder-box linings, automobile fittings such as edging used around running-boards, etc.; oil cans, grease guns; tire valve boxes and certain parts of tire valves; lighting fixtures, electric fixtures, switch plates, plug-casings and socket casings; base metal for silver- and nickel-plated articles; lead pencil ferrules and tips.

4. *Miscellaneous.*—Dials, grain screens, casket linings and cremation urns, shoe nails, file protectors and name plates.

In the consideration of these various applications, it may be well to

discuss certain of them in detail and introduce merely a few words of explanation in other cases.

The use of rolled zinc for boiler plates and hull plates, as well as for shavings in cyaniding, is well known. In certain types of primary batteries, rolled zinc elements are being successfully used. Rolled zinc is used extensively for the casings of dry batteries. The cases for the No. 6 dry cell are built up and soldered. The seamless drawn zinc battery shell, which has lately found application in the smaller batteries for pocket lights, has caused considerable favorable comment. The steps followed in the drawings of a case, together with the finished case, are illustrated in Fig. 15, along with a soldered No. 6 case.

The use of zinc for replaceable electric fuses has been quite extensive of late. Metal for this purpose must be accurate as to gage and have uniform electrical properties. Rolled zinc with a minimum of impurities is probably best for this purpose, due to the tendency of the finished

FIG. 16.—STRIP ZINC ROOFING MATERIAL.

article always to fail at the proper amperage. Zinc is non-magnetic and for this reason finds application in the form of casings for electrical measuring instruments, and other electrical apparatus.

The relative permanency and anti-staining properties of zinc have long been recognized abroad. Zinc has been used for metal roofs on the Continent for a number of years. These roofs have been described on many occasions. The foreign method of application, together with the probable life, are excellently set forth in an article by W. H. Seaman in the *Engineering and Mining Journal*, Oct. 5, 1918.

Considerable prejudice against zinc exists in this country among tinsmiths, due mainly to a lack of knowledge of the physcial properties of the metal.

In the first place, there is some opinion that zinc cannot be soldered. Reference to the manufacture of dry batteries will clearly show the fallacy of this. Second, zinc is considered too brittle to work extensively. This is true of some grades of sheet zinc. Properly rolled Horse Head strip, however, is far from brittle, as shown by the deep drawing illus-

trated in Fig. 17 and by the bends made in a strip of metal according to Fig. 16. Third, a proper conception of the expansion and contraction of the metal at extremes of temperature is necessary in order to properly lay zinc on a roof. This latter subject is covered in a number of contributions to foreign and domestic trade papers.[24] Recently, The New Jersey Zinc Co. has erected a metal shingle zinc roof on a two-family dwelling at Palmerton, Pa. The shingles, valleys, ridge rolls, gutters and leaders were all fabricated from zinc by the National Sheet Metal Roofing Co., of Jersey City, N. J.

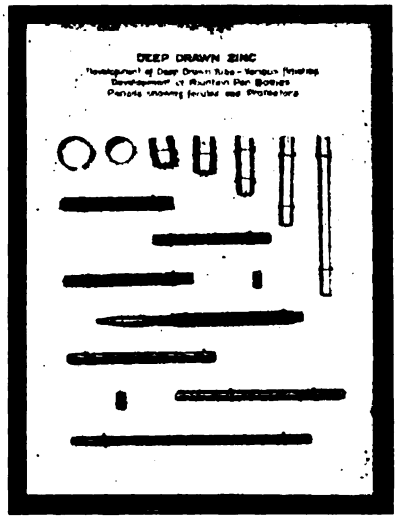

FIG. 17.—DEVELOPMENT OF DEEP DRAWN ZINC TUBE.

Zinc gutters are used quite extensively on buildings having stone copings. The salts running from a gutter made of copper would badly discolor the stone, whereas the common salts of zinc are white and no staining results.

Probably this non-staining feature of zinc was first appreciated by the corset manufacturers, for brass corset eyelets and brass tips for corset steels soon make the garment unsightly and unfit for wear. It has been found that Horse Head zinc possesses superior non-staining qualities and also superior drawing qualities; it is, therefore, demanded by many corset manufacturers for their eyelets.

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[24] Different Kinds of Zinc Roofing, Vieille-Montagne, *Pamphlet* 25, Liége, 1897;
Various Systems of Roofing, *Instructions pratique*, Vieille-Montagne (1900);
W. H. Seaman: Sheet Zinc for Roofing, *Eng. & Min. Jnl.* (1918) **105**, 620–639;
Use of Zinc by Sheet Metal Contractors *Metal Worker* (1919) **91**, 58;
Wm. Neubecker: Covering Dome-shaped Roofs, *Metal Worker* (1919) **91**, 575–577;
Wm. Hutton: Zinc as a Roof Covering, *Metal Worker* (1919) **91**, 370–371;
Practical Talks on Zinc Roofing, *Practical Sheet Metal Work*, **3**, 93–103.

Zinc has been quite extensively used for weather stripping, but objections have been raised against strip zinc due to alleged poor bending properties. As evidenced by the severe bends illustrated in Fig. 16, properly rolled Horse Head strip is entirely suitable for this purpose. Zinc glaziers' points have long been used; their superiority over galvanized steel need only be mentioned in passing.

FIG. 18.—LARGE TUBE AT LEFT ELECTRICALLY WELDED. OTHER TUBES DRAWN AFTER CUPPING.

Recently zinc has been applied to the manufacture of automatic washing machines under conditions which cannot fail to severely test the properties of the metal. As an indication of the value of zinc for this service it is to be remembered that rolled zinc has been used on washboards for several generations.

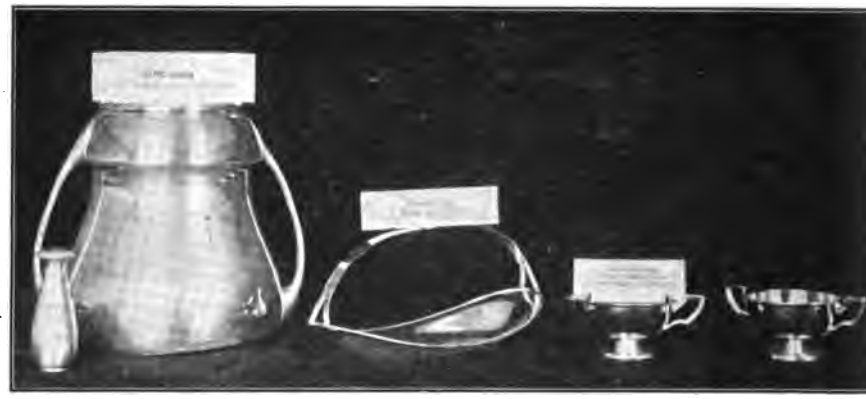

FIG. 19.—SPUN AND POLISHED ARTICLES ON LEFT. DRAWN AND SILVER-PLATED ARTICLES ON RIGHT.

Large quantities of strip zinc are being used to manufacture weather resisting tags, the printed matter being stamped on by a machine similar to the addressograph. Rolled zinc is also extensively applied in the manufacture of boxes used for shoe polish.

It has long been thought impossible to satisfactorily form many articles from sheet zinc, but experimental work has developed a rolled

product which will admirably withstand deep drawing. A simple draw is the well-known Mason jar top.

FIG. 20.—MISCELLANEOUS APPLICATIONS OF ROLLED, FORMED, SPUN AND PLATED ZINC.

One of the larger manufacturers of lead-pencils has lately made use of rolled zinc for lead pencil tips and the ferrule placed on the end of the

FIG. 21.—ZINC ROD AND WIRE.

pencil to hold the eraser. These shapes were formed by drawing zinc into quite a deep tube as illustrated in Fig. 17.

A recent experimental development has been the manufacture of

seamless zinc tubing, as illustrated in Fig. 18. This tubing was made by the following process: A blank 6 in. in diameter and 0.065 in. thick was drawn on presses to a cylinder, the bottom sheared out, and the tubing completed by drawing on a bench through dies over a steel arbor. During these operations no annealing is necessary.

Zinc has been successfully spun and formed into electric lighting fixtures. Ornamental metal doors and other similar objects have been successfully manufactured from zinc. Certain doors which have been under observation are exposed to the outside atmosphere and polishing with a neutral polish at intervals serves to maintain their luster.

One would naturally suggest the use of strip zinc as a base metal for plated ware. Special selected metal is best for this purpose. Some silver-plated pieces are shown in Fig. 19.

A number of the miscellaneous applications of rolled, formed, spun, and plated zinc are illustrated in Fig. 20. These require no special comment.

During the war, the manufacture of ¾-in. diameter zinc rod was requested for use in certain parts of field wireless equipment. A pulled section of this rod having a tensile strength of 20,300 lb. to the sq. in. and an elongation of 54.5 per cent. in 8 in., is shown in Fig. 21. Later, the semi-commercial manufacture of rod and wire between 0.750 in. and 0.005 in. in diameter was successfully accomplished The rod has found application in the manufacture of parts on automatic screw machines, while the wire is used for shoe nails, for the fuse wire of fuse plugs, etc.

An interesting development is illustrated at the extreme left of Fig. 18. Two rectangles of rolled zinc were formed in a press to the cross-section of a semi-circle. These two sections were then electrically welded into the finished tube as shown.

DISCUSSION

W. H. PORTH, New York, N.Y.—I would like to ask what effect segregation of lead would have upon the corrosion of sheet zinc; also what effect would abnormal percentages of iron have upon the ductility of sheet zinc? One of our difficulties seemed to be that the cells, when standing on the shelf, corroded. We have attributed this to local action in the zinc sheet. We would like to know whether the segregation of these impurities in this sheet zinc will have any effect on the local action occurring in sheet zinc. Lately we have had difficulty in punching some sheet zinc, in that the sheets split in the die. The section that split seemed to have an abnormallly high percentage of cadmium and iron; would that cause it to become brittle?

C. H. MATHEWSON.—Iron is one of the most unwelcome impurities when high ductility is the principal requirement in rolled zinc. High iron would certainly affect the drawing qualities adversely. Abnormally high percentages of cadmium localized in portions of the rolled sheet would probably produce hard spots and cause brittleness. I don't feel competent to definitely answer questions as to the corrosion of rolled zinc since we have not completed any very exhaustive series of tests along that line. In general, anything that tends to bring about local variations of concentration in metal is disadvantageous from the standpoint of corrosion, and I should regard pronounced segregation of lead as disadvantageous on general principles.

W. H. PORTH.—To us, that corrosion seemed to be more evident with sheet zinc that was of rather high purity than on zinc that was not so pure; that is, contained less lead.

F. G. BREYER, Palmerton, Pa.—May I ask, when you speak of corrosion, was that the result of a corrosion test?

W. H. PORTH.—No, it was not. We judge entirely by the shelf-life deterioration of a dry cell.

F. G. BREYER.—The trouble with the battery shelf deterioration is that there are so many other things that enter into it besides the metal itself. We should develop a satisfactory test that has fewer variables in it and which can be exterpolated to shelf life.

Five Foundry Tests of Zinc Bronzes

BY C. P. KARR,* PH. B., WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

FOR several years, the Bureau of Standards has been working in coöperation with an Advisory Committee on non-ferrous metals on various phases of the production and testing of zinc bronzes. The work has dealt especially with the type of metal known as "Admiralty bronze" in England and as "Government bronze" in this country and consisting of 88 copper, 10 tin, and 2 zinc. Several reports have been made on this subject and these should be considered in connection with this paper.[1]

FIRST SERIES OF FIVE FOUNDRY TESTS

A very brief summary of the first series of five foundry tests has been made,[2] but for the sake of clearness the results are given here in different form. The five foundries coöperating in this investigation were: Ohio Brass Co., Mansfield, Ohio; Titanium Alloy Mfg. Co., Niagara Falls, N. Y.; Packard Motor Car Co., Detroit, Mich.; National Cash Register Co., Dayton, Ohio; Bureau of Standards, Washington, D. C. The object of the work was to determine whether uniform results could be obtained with this alloy in different foundries working under definite instructions.

One of the participating foundries prepared, from virgin metal, a stock of ingots of the composition 88 copper, 10 tin, 2 zinc, and at the same time poured nine test bars from this melt of virgin metal. The results of the physical tests of these bars are shown in Table 1. Examination of this table shows that the highest and most nearly uniform results were obtained when the virgin metal was cast flat in chill molds and the lowest and most variable results were encountered when it was cast vertical in green-sand molds. In this, as in all other tables, the mean deviation was obtained by the usual method of taking the average of the differences of the individual values from the average values.

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[1] Report of Work Done at the Bureau of Standards on Non-ferrous Metals during 1913. *Trans.* Am. Inst. Met. (1913) 7, 252–287; Standard Test Specimens of Zinc Bronze. U. S. Bureau of Standards *Tech. Paper* 59 (1916); Report on a Series of Comparative Tests of Zinc-bronze Standard Test Bars. *Trans.* Am. Inst. Met. (1916) 10, 77.

[2] Last reference above.

A part of the ingots were sent to each of the five foundries with instructions that test bars be made in various stated ways, using not over 25 per cent. of gates and runners as scrap and maintaining pouring temperatures between 1100° and 1200° C. The instructions specified also that Albany No. 2 sand should be used for molds; but for skin-dried molds, allowed the use of any facing sand or binder commonly used in good foundry practice.

TABLE 1.—*Five Foundry Tests, Series* 1, *Virgin Metal. Composition of charge:* 88 *copper,* 10 *tin,* 2 *zinc. Averaged results of physical tests with mean deviations*

Method of Casting	Number of Specimens	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Number of Specimens Containing Flaws	Number of Specimen Breaking Gage
Flat, skin dried sand	3	40,400 ±1,600	16.0 ±2.0	14.8 ±1.5		1
Vertical, green sand	3	38,000 ±3,300	9.7 ±3.8	6.3 ±3.2		1
Vertical, skin dried sand	3	38,000 ±3,300	12.3 ±2.9	9.7 ±3.1		1
In chill	3	44,100 ±2,900	27.3 ±2.4	23.7 ±2.3	1	

TABLE 2.—*Five Foundry Tests, Series* 1, *First Remelt. Composition of charge:* 88 *copper,* 10 *tin,* 2 *zinc. Averaged results of physical tests with mean deviations*

Method of Casting	Number of Specimens	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Number of Specimens Containing Flaws	Number of Specimens Breaking Outside Gage Limits
Flat, green sand	15	36,590 ±3,190	12.0 ±4.2	10.1 ±3.6	2	9
Flat, dry sand	15	37,000 ±2,800	11.0 ±2.6	8.9 ±2.1	3	7
Vertical, green sand	15	33,830 ±4,700	9.9 ±4.0	9.2 ±3.7	4	5
Vertical, dry sand	15	32,130 ±5,570	9.7 ±4.6	9.1 ±3.3	10	5
In chill	21	42,100 ±4,800	25.0 ±8.8	19.7 ±5.8	2	6

The instructions as to pouring temperatures were not adhered to strictly by some of the foundries for the pouring temperatures varied

from 1050° to 1350° C. Although not specified in the instructions, all sand-cast specimens were supposed to be 4½ in. (11 cm.) long and ⅝ in. (1.5 cm.) diameter in the center sections and all chill specimens were supposed to be 14½ by 2 by 1¼ in. (37 by 5 by 3 cm.). The test bars made actually varied in length from 4½ in. to 14 in. in length and from ⅝ in. to ¾ in. in diameter, center section. In addition to these variations in pouring temperatures and size of test bars, a large number of the test bars showed flaws and many others broke outside of the gage limits when being tested. For these reasons, the results of the tests have less significance than was expected. They are valuable mainly as an example of the extreme care that must be taken to keep conditions uniform in conducting comparative tests on metal so sensitive to slight variations in method of working as Government bronze is known to be. The results are shown in Table 2, in which the superiority of the chill casting stands out.

Effect of Heat Treatment

In order to determine the effect of heat treatment on the properties of this alloy, a second remelt was made in the foundry of the Bureau of Standards. The results are shown in Table 3. Examination of this table

Table 3.—*Five Foundry Tests, Series I, Second Remelt. Composition of charge:* 88 *copper,* 10 *tin,* 2 *zinc. All specimens were cast approximately to size. Averaged results of physical tests*

How Cast	Heat Treatment	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
Flat, green sand.....	Quenched at 700° C	41,550	29	12
	Annealed at 700° C.	44,000	39	25
	None	41,230	17	13
Flat, skin dried sand....	Quenched at 600° C.	45,300	37	22
	Annealed at 600° C.	46,610	39	27
	None	41,790	27	19.6
Vertical, green sand.....	Quenched at 700° C.	43,780	39	22.7
	Annealed at 700° C.	44,550	46	29.5
	None	42,000	27	10.6
Vertical, skin dried sand.	Quenched at 600° C.	47,940	38	13
	Annealed at 600° C.	49,380	35	17
	None	39,850	25	17.5
In chill.....	Quenched at 600° C.	29,640	17	11
	Quenched at 700° C.	32,890	25	16
	Quenched at 700° C.	29,000	22	3
	Annealed at 600° C.	29,800	19	13
	Annealed at 700° C.	27,900	19	10
	None	31,875	5	3.5
	None	25,300	5	2.0
	None	26,000	5	2.5

TABLE 4.—*Five Foundry Tests. Composition of charge:* 88 *copper,* 10 *tin,* 2 *zinc. Showing effect of continued remelting. All melts except that of virgin metal were made at the Bureau of Standards. Averaged results of physical tests with mean deviations*

Method of Casting	Number of Melt	Number of Specimens	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
Flat, green sand....	1				
	2	3	38,200	10.0	8.5
			±800	±0.6	±1.1
	3	3	42,600	7.3	11.5
			±1,000	±0.6	±1.0
	4	3	40,100	9.0	10.5
			±3,800	±2.0	±3.3
Flat, skin dried sand	1	3	40,400	16.0	14.8
			±1,600	±2.0	±1.5
	2	3	40,400	11.0	8.1
			±600	±1.3	±1.2
	3	3	42,800	14.0	20.0
			±1,300	±0.3	±5.0
	4	3	43,100	15.0	18.0
			±2,400	±3.0	±4.0
Vertical green sand.	1	3	38,000	9.7	6.3
			±3,300	±3.8	±3.2
	2	3	38,200	15.0	13.5
			±2,300	±0.6	±3.9
	3	3	36,500	4.7	10.0
			±2,000	±0.2	±0.3
	4	3	35,500	9.0	8.0
			±1,300	±1.6	±2.0
Vertical, skin dried sand	1	3	38,000	12.3	9.7
			±3,000	±2.9	±3.1
	2	3	35,700	12.3	10.3
			±2,600	±3.5	±3.8
	3	3	37,500	8.5	13.0
			±1,950	±2.0	±2.3
	4		35,400	9.0	9.5
			1,000	±2.0	±1.3
In chill.....	1	3	44,100	27.3	23.7
			±2,900	±2.4	±2.3
	2	3	43,800	20.0	16.2
			±3,500	±6.0	±5.8
	3	3	31,600	4.0	6.0
			±3,700	±0.8	±3.1
	4	6	25,600	1.8	2.6
			±3,200	±0.3	±1.1

shows that the physical properties of the specimens cast in sand were improved somewhat by heat treatment, annealing being more effective than quenching. In the specimens cast in chills, the ductility of the metal was increased markedly by heat treatment, but the tensile strength was not altered materially. The sand-cast specimens of the second remelt are better than the chill castings of the first or second remelts. These results are in general accord with those of other investigators.[3]

Effect of Continued Remelting

To determine the effect of continued remelting on the alloy, three remelts of the same metal were made at the Bureau of Standards. The pouring temperatures being kept at about 1100° C. The results are shown in Table 4. In the case of specimens cast in chills, the virgin metal gave the highest values and there was a marked falling off in strength wtih continued remelting. No marked effect due to remelting is noticeable in the specimens cast in sand. This may be due to the maintenance of a low pouring temperature for it is well known in foundry practice that Government bronze tends to deteriorate after two or three meltings.[4]

Second Series of Five Foundry Tests

After discussion in committee, it was decided to repeat the first remelt series of tests conducted by the five coöperating foundries but to use longer test bars cast in molds made from core sand and linseed oil and baked in a core oven. These molds were all made for pouring flat and were all provided with reservoir gates, the gates being made in green sand. The shape and dimensions of the mold and gate are the design of Mr. McKinney of the Naval Gun Factory and are shown in Fig. 1. It was decided further to conduct a similar series of tests on ingots of the composition 88 copper, 8 tin, 4 zinc. The pouring temperatures varied somewhat, from 1100° to 1300° C., due to established practice in the various foundries, but otherwise conditions were kept as uniform as possible. The care taken in making this series of tests was justified by the facts that none of the specimens broke outside of the gage limits while being tested and none showed flaws. The results of the physical tests are shown in Tables 5 and 6.

[3] E. S. Shepherd and G. B. Upton: *Jnl. Phys. Chem.* (1905) **9**, 441–476.
St. Etienne: Soc. de L'Ind., *Stoye Memoriale* (Mch., 1911) 138.
H. S. and J. S. G. Primrose: *Jnl.* Inst. Met. (1913) **9**, 161.
M. S. Guillet: *Rev. de Met.* (1905) **2**, 118.
John Dewrance: *Jnl.* Inst. Met. (1914) **11**, 216.
C. P. Karr and H. S. Rawdon: *Tech. Paper*, U. S. Bureau of Standards.
H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1918) **19**,155.

[4] Decourcy Brown: *Trans.* Am. Inst. Met. (1914) **8**, 63. *Brass World* (1913) **9**, 176.

TABLE 5.—*Five Foundry Tests, Series II. Composition of charge:* 88 *copper,* 10 *tin,* 2 *zinc. All specimens were cast approximately to size, horizontal, in baked core-sand molds with reservoir gates. Averaged results of physical tests with mean deviations*

Foundry	Number of Specimens	Proportional Limit	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
A	6	11,250	33,600	22.3	18.0
		±1,300	±1,400	±1.1	±2.0
B	6	13,100	43,100	39.7	24.3
		±1,050	±3,350	±4.5	±2.2
C	6	13,750	42,600	31.3	24.6
		±600	±2,200	±5.0	±3.4
D	6	10,000	31,100	17.8	15.8
		±1,500	±2,500	±4.4	±4.3
E	6	13,100	43,800	25.1	22.5
		±900	±1,950	±4.5	±4.5
Total	30	12,200	38,900	25.3	21.0
		±1,600	±5,250	±5.9	±4.7

TABLE 6.—*Five Foundry Tests, Series II. Composition of charge:* 88 *copper,* 8 *tin,* 4 *zinc. All specimens were cast approximately to size, horizontal, in baked core-sand molds with reservoir gates. Averaged results of physical tests and mean deviations*

Foundry	Number of Specimens	Proportional Limit	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
A	5	12,400	46,000	40.0	30.0
		±1,700	±1,600	±3.0	±1.7
B	6	11,900	43,300	36.0	28.0
		±900	±1,850	±4.5	±4.5
C	6	10,200	34,600	29.5	24.4
		±1,000	±2,400	±5.2	±3.0
D	6	9,600	36,400	31.5	23.6
		±1,400	±2,400	±5.7	±3.4
E	3	11,300	35,900	15.3	14.6
		±2,900	±3,750	±7.1	±5.6
Total	26	11,000	39,400	32.0	25.0
		±1,650	±4,200	±7.0	±4.6

Examination of these tables shows that even with rather carefully standardized methods of making test bars of this type of alloy, there may be considerable variation in the physical properties of bars produced in the same foundry and greater variation in those from different foundries. The results for the alloy 88 copper, 8 tin, 4 zinc compared with

those for 88 copper, 10 tin, 2 zinc indicate that it is a somewhat more ductile metal than the 88–10–2 mixture, has about the same tensile strength, but a lower proportional limit. It is interesting to note that some of the foundries that produced specimens with highest values with the 88–10–2 alloy made bars with the 88–10–4 alloy that gave some of the lowest values, and vice versa. This is probably due, largely, to the pouring tempera-

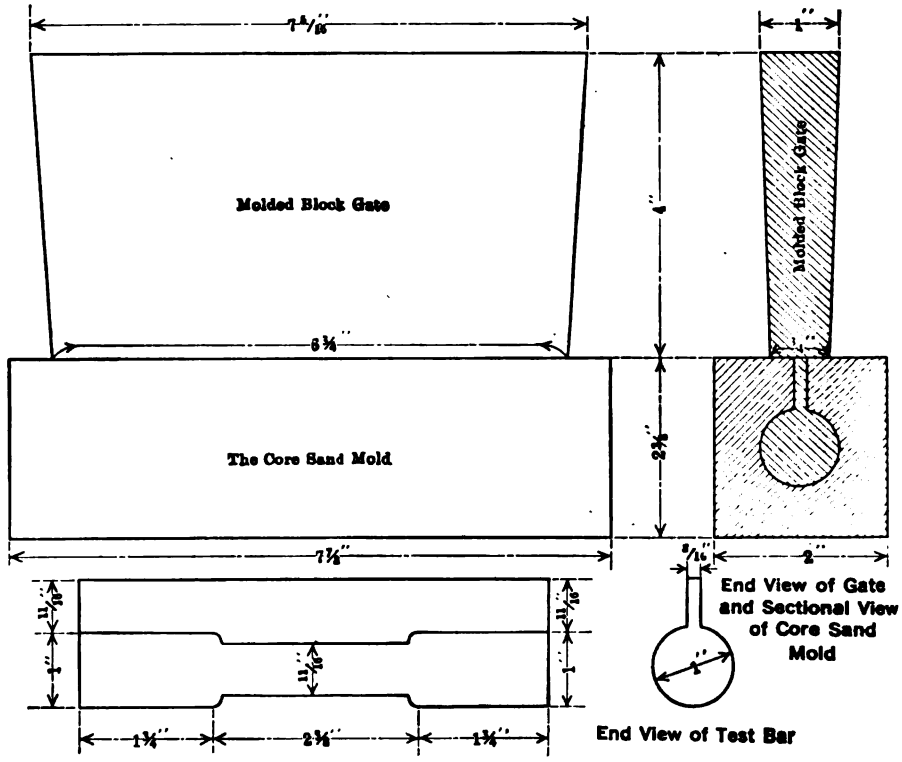

FIG. 1.—TYPE OF TEST BAR USED IN SECOND SERIES.

tures used in the foundries in question being more suitable for one alloy than for the other.

SUMMARY

In conducting comparative tests of alloys of the Government bronze type, great care must be taken to keep uniform all conditions affecting the quality of the finished castings, such as composition of charge, pouring temperature, shape and size of test bars, kind of mold used, method of pouring and gating, etc.

With rather carefully standardized methods of making test bars of this type of alloy, considerable variation in physical properties of test

specimens from the same foundry are to be expected and greater variation in those from different foundries.

The two alloys studied gave the following average values for test bars cast approximately to size horizontal in baked core-sand molds with reservoir gates.

Composition	Number of Specimens	Proportional Limit	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
88 Cu, 10 Sn, 2 Zn.....	30	12,200	38,900	25.3	21.0
		±1,600	±5,250	±5.9	±4.7
88 Cu, 8 Sn, 4 Zn.....	26	11,000	39,400	32.0	25.0
		±1,650	±4,200	±7.0	±4.6

DISCUSSION

W. M. CORSE, Mansfield, Ohio.—We have sometimes seen in individual tests ultimate tensile strengths as high as 55,000 lb. per sq. in. being attained under electric furnace practice. These results, of course, average much lower than that, but with better methods of melting, can we hope to get the strength up to somewhere near the figure attained by these individual tests?

C. P. KARR.—Yes, because with the electric furnace you can lessen the oxidation by means of the impurities always found in the melting. But one of the most important things in making 88–10–2 bronze of this class is to use a core-sand mold with a very open grain, so that the gases carried down will have a chance to escape through the sand, and thus increase the tensile strength.

THE CHAIRMAN (W. H. BASSETT, Waterbury, Conn.).—Do I understand that pouring temperatures of 1120° to 1270° gave equally good results and with variations beyond the temperatures either way, the properties are affected?

C. P. KARR.—If you go much below 1100° you will not get very high results. If you go above 1270° you will have some of the oxidation products in the metal. Professor Carpenter carried my experiment further and heated some of the metal up to 1450° and allowed the metal to cool in the pot to somewhat below 1270°. The original valuable properties of the metal were restored, while the metal was cooled back within that temperature range, which was certainly a very remarkable discovery.

W. M. CORSE.—With 88–10–2 bronze in very thin castings, it seems very difficult to get the elongations specified by the Navy specifications, 14 and 15 per cent. I would like to ask Mr. McKinney if he has had similar experiences with thin castings of this metal?

P. E. MCKINNEY,* Washington, D. C.—Of all the metals we handle, probably the red bronzes, containing approximately 10 per cent. of tin, are the most delicate and susceptible to slight changes in foundry practice, and the range is so very close that the restricting of the size of the gate or the increasing of the temperature by very slight margins will very frequently destroy the entire object sought; that is, the elongation will suddenly drop to nothing and you will have a fracture either in the casting, or the test bar, that is entirely crystalline and apparently rather segregated. I think Mr. Karr's paper has shown very clearly that very small changes in practice effect big changes in the results obtained, a great deal more than in the case of some of the bronzes that don't have the excess of free eutectic that will freeze out and give us erratic grain conditions and intercrystalline cracks and various troubles of that kind. Mr. Corse's question requires every individual casting to be considered on its own merits, and foundry practice developed for that casting that is typical of that casting alone.

Mr. Karr states that the test bar used in the experiments was a design of my own. I would like to correct that impression, because while we have used it, the design is practically identical with the original Webert bar.

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* Chemist and Metallurgist, U. S. Naval Gun Factory.

Physical Properties of Nickel*

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(Philadelphia Meeting, September, 1919)

FOREWORD

THE literature dealing with the physical constants of nickel is so fragmentary and unrelated that a synopsis presents unusual difficulties. It is only within the last few years that investigators have understood the importance of placing on record not only the determinations they have made but also the composition, physical treatment, and past history of the material investigated. For this reason much of the earlier literature is valueless. Determinations have been made of the same physical constants on samples differing widely in origin, composition, and treatment, and the results differ widely among themselves.

In the first place nickel is almost as flexible a term as steel. Its physical properties are widely influenced by its composition and treatment. It absorbs large quantities of gases and is exceedingly difficult to prepare in a state of chemical purity comparable to gold, silver, or copper. It is vitally affected by thermal and mechanical treatment. Hence in the following pages the recorded literature, where quoted, must be accepted with a certain reserve and used, as far as possible, as a check on later observations, in which these important factors are noted. In every case where new determinations are given, an attempt has been made to record all available information concerning the composition and treatment of the material used so that the data may serve as stepping-stones toward a wider knowledge of the properties of the metal.

As this synopsis is an attempt by men of metallurgical training to do what should long before have been done by physicists, it is to be expected that certain errors may have crept in. Any corrections or suggestions

* The preparation of this paper was begun by the late David H. Browne and myself some years ago in an endeavor to collect for our own use the best available data on the more valuable properties of nickel. The widely scattered sources of much of the material, together with the fact that much was unpublished, made it seem advisable to publish it for general use. The work was interrupted by Mr. Browne's death and greatly delayed by the pressure of work entailed by the war. The call for such data in easily available form has become greater as time passes and I have accordingly consolidated and rewritten it into the following necessarily brief summary.

JOHN F. THOMPSON.

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cementation, the nickel solution can be electrolyzed for the production of metallic nickel. This nickel may be sold directly in the form of nickel cathodes, or it may be remelted and sold as ingots.

The second process is the Mond,[4] in which the Bessemer matte, which contains copper, nickel, sulfur, and a very small amount of iron, is roasted. The copper is in part removed by leaching with sulfuric acid, forming copper sulfate; the residue, containing nickel oxide with some copper oxide and iron, is reduced at a low heat to a finely divided metallic powder. This is carefully protected from contact with the air and carbon monoxide is passed over it at ordinary room temperatures. This carbon monoxide dissolves part of the nickel, forming nickel carbonyl, which is a vapor at the temperature employed. The mixture of gases, carbon monoxide and nickel carbonyl, is passed through an apparatus containing small shot nickel heated to about 300° C. At this temperature, nickel carbonyl splits up into monoxide, which is led back over the metallic powder, and metallic nickel which forms a coating over the nickel shot. The nickel shot is alternately exposed to and withdrawn from the action of this gas, and in this way a series of concentric layers of nickel are built up around the original nucleus, like the coats of an onion. The metal may be sold in this form, or it may be melted into ingots. Mond shot may readily be recognized; hammering upon an anvil will break open the various coatings and show the characteristic structure.

The third method, whereby most of the nickel is produced in the United States, is known as the Orford Process.[5] The Bessemer matte is melted with salt cake or niter cake. These are both forms of sodium sulfate, which in the furnace reduce to sodium sulfide. This sodium sulfide forms, with the copper, a soda-copper matte of low specific gravity. The molten material from the furnace is allowed to cool in pots. After the material is cold the top part, which contains the most of the copper with the soda and some nickel, splits off from the bottom, which contains most of the nickel with some copper. Several treatments are required to produce on the one side a crude sulfide of copper and soda and on the other side a crude sulfide of nickel. The sulfide of copper and soda, known as "tops," goes to copper converters where the copper is recovered as blister copper. The sulfide of nickel, known as "bottoms," goes through a series of roastings and leachings and finally becomes nickel oxide. This is reduced with charcoal at a heat above the melting

[4] Roberts-Austen; *Proc.* Inst. Civ. Engrs., **135**, 29.

[5] John L. Thomson: U. S. Pat. 489882.

R. M. Thompson: *Min. Ind.* (1892) **1**, 357. A. Monell: U. S. Pat. 802012, Oct. 17, 1905.

R. R. Maffett: U. S. Pat. 802148, Oct. 17, 1905. *Min. Ind.* (1905) **14**, 466.

(The word Orford in this paper refers to the Orford Works of the International Nickel Co.)

point of nickel and is cast into blocks or poured into water to form shot.

For the production of the highest grade nickel, a portion of the metal is cast into anodes. From these anodes pure electrolytic nickel is deposited on cathodes. These may be sold uncut, or they may be cut into small pieces for crucible melting, or they may be remelted and cast into ingots for rolling.

This brief sketch of the metallurgy[6] shows that what is called nickel may be as follows:

1. Grains, cubes, rondelles, or powder reduced at a low heat from nickel oxide and not fused in process of manufacture.

2. Nickel deposited as concentric coats from nickel carbonyl and not fused in process of manufacture.

3. Nickel deposited by some electrolytic method in the form of a cathode and not fused in process of manufacture.

4. Nickel in the form of shot or blocks made by reducing nickel oxide at a temperature above the melting point of nickel and casting into shot or blocks without deoxidation.

5. Malleable nickel made by treating molten nickel with some deoxidizer before casting into molds. This may appear as unworked ingots or as rods, sheet, wire or other commercial forms.

Most of the nickel of commerce falls in class 4.

Forms of Nickel Produced by the International Nickel Co.

Shot Nickel.—There are two grades of shot nickel, A and X.

A shot is a high carbon nickel used by anode manufacturers. It has approximately, the composition shown. X shot is a purer material used by the manufacturers of crucible nickel steel and of nickel silver. Its approximate analysis is shown. *Ingot nickel* is almost identical in composition with X shot. It is sold in 25-, 50-, and 100-lb. ingots and is used in the manufacture of open-hearth and electric-furnace steel.

Electrolytic Nickel.—Electrolytic nickel is approximately as given. It is sold in cathodes 24 by 36 in. (60 by 91 cm.) weighing about 100 lb.

A Shot Nickel

	Per Cent.
Nickel	98.40
Iron	0.60
Copper	0.25
Carbon	0.50
Silicon	0.25
Sulfur	0.06

[6] See Barlow's Report, Part H, *Ann. Rept.* Geol. Survey of Canada (1904) 14. Coleman: Nickel Industry, Can. Dept. Mines (1913).

X Shot Nickel

	Per Cent.
Nickel	98.90–99.00
Iron	0.45–0.55
Copper	0.15–0.25
Carbon	0.18
Silicon	0.15
Sulfur	0.035

Electrolytic Nickel

	Per Cent.
Nickel	99.80
Iron	0.15
Copper	0.05
Carbon	0.0
Silicon	0.0
Sulfur	0.0

(45 kg.) or is cut into smaller squares for convenience. It is used by the manufacturers of high-grade silver and cupro-nickel alloys.

Malleable Nickel.—Malleable nickel, intended for rolling into sheets or rods or for drawing into wires, is made in various grades according to the purpose for which it is destined. All malleable nickel is treated before casting into ingots with some deoxidizer, such as metallic magnesium. A very small amount of this metal introduced into a crucible of molten nickel removes any oxygen that the nickel may contain and is at the same time itself removed as oxide of magnesium. If nickel were not so treated it could not be rolled. Some consumers desire the additions of metallic manganese also; this remains in the finished nickel and makes it more suitable for certain uses.

Typical Analyses of Grades of Malleable Nickel

Grade A*	Per Cent.	Grade C†	Per Cent.
Nickel	98.90 to 99.00	Nickel	96.50 to 97.00
Iron	0.50	Iron	0.50 to 1.00
Manganese	0.20 to 0.35	Manganese	1.50 to 2.00
Copper	0.18	Copper	0.20
Carbon	0.10	Carbon	0.20
Silicon	0.10 to 0.20	Silicon	0.10 to 0.20
Sulfur	0.025	Sulfur	0.035

* Made from specially refined nickel.

† High-manganese nickel.

Grade D.—Grade D is a high-manganese nickel made with varying manganese contents for a variety of purposes. The impurities are the same in kind and amount as in Grade A.

All metallic nickel produced by the Orford process contains about 0.4 per cent. cobalt. The properties of this metal are so closely analogous to nickel that the effect of this small amount of cobalt is not discernible.

Unless otherwise stated in this paper, the cobalt present is considered as nickel and reported as nickel.

Analyses of Various Kinds of Nickel

Table 1 shows the composition of various kinds of nickel. The results are not to be taken as averages but represent, solely, the analyses of individual samples.

Atomic Weight

The International Committee on Atomic Weights, for 1913, places the atomic weight of nickel at 58.68. This figure is given in Landolt-Bornstein ("Phys. Chem. Tab.," 1912) and is taken from the table of atomic weights as revised by the committee, which consists of Messrs. F. W. Clarke, T. E. Thorpe, W. Ostwald and G. Urbain. A paper by Richards and Cushman[7] gives a chronological list of research on the atomic weight of nickel as follows:

1826, Rothoff	59.1
1852, Erdmann and Marchand	58.2 –58.6
1856, Deville	58.85
1857, Schneider	58.07
1858, Marignac	58.4 –59.29
1860, Dumas	59.02
1863, Russell	58.74
1866, Sommaruga	58.03
1867, Winkler	59.45
1871, Lee	58.01
1883, Baubigny	58.73
1886, Zimmermann	58.71
1890, Mond, Langer and Quincke	58.58
1892, Schützenberger	58.54

The authors describe the method followed and give the results obtained through the analysis of nickel bromide. Sample 1, 58.677; sample 2, 58.683; sample 3, 58.688; sample 4, 58.689. They conclude with a statement of opinion that the atomic weight of nickel cannot be far from 58.69 if oxygen is taken as having an atomic weight of 16.

Specific Gravity

The specific gravity of nickel varies greatly according to its chemical analysis, its physical condition, and the mechanical treatment that it has received. Few, if any of the earlier observers have taken this into account, hence various determinations ranging from 7.94 to 9.25 are quoted.

[7] *Chem. News* (1897) **76**, 284, 308.

TABLE 1.—*Composition of*

Name	Source	Form	Cu	Ni and Co	Co	Fe
Norway nickel	V. Hybinette	Electro	0.06	99.52	0.89	0.36
Canadian nickel	D. H. Browne	Electro	0.010	99.80	....	0.12
Orford nickel	International Nickel Co.	Electro	0.01	99.84	....	.....
Orford nickel	International Nickel Co.	Electro	0.02	99.80	0.80	0.14
Electrolytic nickel	Hybinette Process	Electro	0.10	98.75	....	0.50
Nickel shot	U. S. Nickel Co.	Shot	0.052	98.62	....	0.55
Nickel shot	U. S. Nickel Co.	Shot	0.06	98.98	1.01	0.58
Mond nickel	L. Mond (England)	Shot	0.03	99.36	0.06	0.39
Metallic nickel	U. S. Nickel Co.	Shot	0.05	98.20	....	0.80
Mond nickel	Mond Nickel Co.	Shot	None	99.80	None	.....
Mond nickel	Mond Nickel Co.	Shot	0.008	99.92	None	0.040
Nickel shot	International Nickel Co.	A Shot	0.15	98.65	0.80	0.50
Nickel shot	International Nickel Co.	X Shot	0.15	99.05	0.80	0.47
Nickel shot	International Nickel Co.	A Shot	.....	98.60	....	0.50
Nickel shot	International Nickel Co.	X Shot	0.10	99.08	....	0.46
Mond nickel	L. Mond	.....	.....	99.80	....	.....
Nickel shot	International Nickel Co.	X Shot	0.20	99.00	....	0.50
Nickel cubes	U. S. Nickel Co.	Cubes	0.065	99.16	....	0.32
Metallic nickel	Le Nickel	Cubes	.....	99.41	....	.....
Nickel cubes	.....	Cubes	0.10	+99.00	....	0.23
Nickel cubes	Wiggins	Cubes	.....	99.25	....	.....
Grain nickel	Am. Nickel Works	Grain	0.13	99.17	....	0.51
Mond nickel	Ludwick Mond	Grain	0.014	99.57	....	0.133
Metallic nickel	Le Nickel	Grains	.....	99.38	....	.....
French nickel	Le Nickel	Rondelle	0.112	99.01	....	0.43
Nickel ingots	International Nickel Co.	Ingots	0.11	99.09	0.32	0.65
Nickel ingots	International Nickel Co.	Ingots	0.13	99.10	0.80	0.50
Metallic nickel	Le Nickel	Brick	.....	99.60	....	.....
Metallic nickel	Le Nickel	Cylinders	.....	99.11	....	.....
Nickel rod	H. Boker & Co.	Rods	0.18	97.58	....	0.38
Electro malleable nickel	International Nickel Co.	Rods	0.10	99.40	0.80	0.30
Malleable nickel A	International Nickel Co.	Rods	.....	99.00	....	0.55
Malleable nickel B	International Nickel Co.	Rods	.....	98.75	....	0.50
Malleable nickel C	International Nickel Co.	Rods	.....	96.75	....	0.75
Nickel tube	H. Boker & Co.	Tube	0.75	97.12	....	0.65
Nickel castings	International Nickel Co.	Castings	.....	98.95	....	0.50
Nickel sheet	Fleitmann Witte & Co.	Sheet	0.12	99.37	....	.....
Malleable nickel	Krupp (Germany)	Sheet No. 1	0.12	99.26	....	0.40
Malleable nickel	Krupp (Germany)	Sheet No. 2	0.10	99.05	....	0.40
Rolled nickel sheet	Baker & Co.	0.001 by 12 in.	0.12	97.99	0.88	0.49
French 25 centimes	France	Coin	0.083	99.26	1.36	4.05
20 centesimi piece	Italy	Coin	0.089	99.23	....	0.31
Arthur Krupp	Berndorf, Austria	Wire rod	0.10	99.20	0.54	0.40
Nickel rod	England	¼ in. wire	0.23	99.13	0.62	0.30
Electro malleable nickel	Driver-Harris	0.081 in. wire	.....	98.47	....	0.80
Gas mantle	Solex Co., Ltd	Wire	.....	98.96	....	0.57
Malleable nickel	Fleitmann Witte & Co.	Wire	.....	98.60	Trace	1.22
Metallic nickel	U. S. Nickel Co.	Various	0.05	99.02	0.12	0.21
Pure nickel	Kalmus & Harper	.....	.....	99.29	Nil.	0.48
Nickel	New Caledonia	.....	0.50	98.00	....	1.60
Nickel	New Caledonia	.....	.....	98.23	....	0.98
N ckel	Basse & Selve	.....	0.10	97.87	1.45	0.45
Nickel	Deloro Mining	.....	0.05	98.00	1.60	0.75

NOTE.—The nickel analyses of some of the samples mentioned by the Royal Ontario Nickel Com-

Various Kinds of Nickel

S	Si	C	Mn	As	Sn and Sb	Insol.	Remarks
.....	.....	.....	....	Trace	Trace	0.015	
0.005	.....	0.005	....	0.01	0.01	0.003	Analyzed by Orford (1908).
Trace	.....	.....	....	.....	.....	.....	Analyzed by Orford (1914).
0.01	.....	.....	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	0.50	0.26					
0.006	0.19	0.16	....	Trace	0.003	.....	
0.002	0.11	0.11	0.09				
0.006	None	0.05	....	.....	.....	.....	Analyzed by Hadfield (1899).
None	0.007	0.030	....	.....	.....	.....	Analyzed by Mond (1915).
0.06	0.15	0.45	....	0.015	0.015	.....	Analyzed by Orford (1914).
0.04	0.10	0.18	....	0.015	0.015	.....	Analyzed by Orford (1914).
0.050	.....	0.50					
0.024	0.05	0.05	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	.....	.....	....	.....	.....	.....	Royal Ontario Nickel Commission.
0.035	0.15	0.018					
.....	.....	0.41					
0.015	0.04	0.176					
0.008	0.12	0.07	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	.....	.....	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	.....	.....	....	.....	.....	1.06	
0.003	.....	0.23	....	Trace	Trace	0.03	
0.010	0.109	0.048	0.01				
0.024	.....	0.037	....	.....	.....	0.068	
0.04	0.01	0.04	....	0.02	0.02	.....	Analyzed by Le Nickel (1905).
0.06	0.10	0.10	....	0.015	0.015	.....	Analyzed by Orford (1914).
0.01	0.104	0.111					
0.006	0.151	0.251					
0.012	0.13	0.19	1.60				
0.015	0.10	0.10	....	Trace	Trace	.....	Analyzed by Orford (1914).
0.025	0.10	0.15	0.15	.....	.....	.....	Typical analyses, Orford Works.
0.025	0.20	0.15	1.75	.....	.....	.....	Typical analyses, Orford Works.
0.03	0.20	0.15	1.75	.....	.....	.....	Typical analyses, Orford Works.
.....	0.10	0.13	1.15				
0.035	.....	0.16	....	.....	.....	.....	Typical analyses, Orford Works.
.....	.....	0.019					
0.024	0.17	0.045	Trace				
0.045	0.16	0.13	0.13				
.....	.....	.....	1.32				
0.05	0.07	0.042	Trace	0.018	0.021		
.....	.....	.....	0.17				
0.01	0.02	0.07	0.22				
0.022	0.06	0.16	0.66				
0.06	0.16	0.13	0.30				
.....	.....	.....	0.15				
.....	.....	.....	0.16	.....	.....	.....	Royal Ontario Nickel Commission.
0.025	0.21	0.39	....	Trace			
0.025	0.042	Nil.	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	0.13	.....	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	0.30	.....	....	.....	.....	.....	Royal Ontario Nickel Commission.
0.05	0.19	Trace	....	.....	.....	.....	Royal Ontario Nickel Commission.
.....	.....	.....	....	.....	.....	.....	Royal Ontario Nickel Commission.

mission are only nickel while in other cases they are nickel plus cobalt.

As nickel reduced by carbon or carbon monoxide to a metallic powder or more or less compact metallic sponge may contain large amounts of carbon and other impurities and may also contain numerous voids, it is evident that nickel in the form of grains, cubes, or rondelles may show a comparatively low specific gravity. These samples stand in the same relation to pure nickel as sponge iron does to pure iron. Hence such values as 7.94 for grain nickel and 8.35 for cast nickel[8] are very misleading. Even pure nickel, if in the form of a fine powder, is of low specific gravity. Mond, Langer and Quincke[9] give 8.2834 at 15.4° C. and 8.2928 at 15.1° C. as specific gravity of pure nickel powder reduced by hydrogen from solutions of nickel made from nickel deposited by the carbonyl process. On the other hand, Fleming[10] gives the specific gravity of pure annealed electrolytic nickel as 8.96 at 18° C.

With the foregoing in mind it is clear that considerable variations in specific gravity are to be expected in nickels of varying composition or of the same composition but produced by different processes. Table 2

TABLE 2.—*Specific Gravity of Nickel*

Reference	Kind of Nickel Used	Sp. Gr.	Temp.
Mond, Langer and Quincke: *Jnl.* Chem. Soc., **57**, 753.	Mond nickel dissolved in acid, precipitated by ammonia, and reduced by hydrogen to metallic powders	8.2834	15.4° C.
		8.2928	15.1° C.
American Nickel Works, private communication.	Whartons grain nickel, 1904, reduced from oxide by charcoal but not melted, a porous metal	7.993	
P. W. Shimer, private communication, 1905.	Orford cast nickel ingot	8.860	62° F.
	Orford cast nickel ingot	8.864	80° F.
	Orford malleable nickel ½-in. plate rolled from remelted electrolytic nickel	8.828	62° F.
	Orford malleable nickel ½-in. plate rolled from remelted electrolytic nickel	8.832	80° F.
	Orford 3-in. bar rolled from cast electrolytic nickel	8.852	62° F.
	Orford 3-in. bar rolled from cast electrolytic nickel	8.863	80° F.
W. Campbell, private communication, 1905.	Orford cast nickel ingot	8.873	62° F.
	Orford malleable nickel 1.2-in. plate rolled from remelted electrolytic nickel	8.844	62° F.
	Orford 3-in. bar rolled from cast electrolytic nickel	8.863	62° F.
Fleming: *Proc.* Roy. Soc. Lond. (1899) **66**, 52.	Pure electrolytic nickel annealed	8.96	18° C.
Copaux: *Ann. Chem. et Phys.* [8] (1905) **6**, 540.	Chemically prepared nickel of exceptional purity reduced by hydrogen and fused	8.80	
		8.64	

[8] Quoted by Huntington and McMillan: "Metals," 376, 1897.
[9] *Jnl.* Chem. Soc., *Trans.* (1890) 753.
[10] *Proc.* Roy. Soc. Lond. (1899) **66**, 52.

gives the results of a number of determinations. A study of all available data on American malleable nickel shows a range from 8.71 to 8.90 with an average of 8.84, which quite closely represents the great bulk of commercial material.

Melting and Transformation Points of Nickel

The melting point of pure nickel, according to the best data extant, is 1451° C. This property has been determined by a number of different observers on samples of varying purity. Those working on samples of the highest purity are in substantial agreement, within a few degrees, on the temperature given.

Nickel has also a single transformation point corresponding to the magnetic transformation point of iron. It is non-magnetic above and magnetic below this point. With increasing copper content, this point is depressed while at the same time the magnetic power weakens until the point is no longer susceptible to determination. Data on this line may be found in the second Guertler and Tammann paper noted in Table 3. This table also gives the result of a number of other determinations of the transformation point.

Table 3.—*Transformation Point of Nickel*

Reference	Remarks	Temperature, Degrees C.
Copaux: *Ann. Chem. et Phys.* [8] (1905) **6**, 508–574.	Cobalt free nickel of utmost purity chemically prepared and melted under hydrogen.....	340
Guertler and Tammann: *Zeit. Anorg. Chem.* (1905) **45**, 205–224.....	.....	325
J. Hopkinson: *Proc. Roy. Soc. Lond.* (1888) **44**, 317.	Impure nickel, Ni 95.15.....	310
Curie: *Compt. Rend.* (1894) **118**, 1134....	.....	340
Pécheux: *La Lumière Électrique* (1910) **16**, 232–239.	Cu 0.20; Fe trace; Co 0.15; C and Si 0.00.....	345
	Cu 0.80; Fe trace; Co trace; C and Si 0.20.....	340
	Cu 0.40; Fe 0.60; Co 0.10; C. and Si 0.15.....	345
	Cu trace; Fe 1.50; Co 0.50; C and Si 0.10.....	335
Guertler and Tammann: *Zeit. fur Anorg. Chem.* (1907) **52**, 25.	Cu trace; Fe 0.47; Co 1.86,.....	320

Specific Heat

In its simplest terms, the specific heat of a metal is the amount or quantity of heat that is required to increase its temperature one degree as compared with the amount of heat required to raise an equal weight

of water one degree. It requires very much less heat to raise the temperature of a certain weight of metal to a given point than is required to raise the temperature of water to the same point, therefore it is said that metals have a low specific heat. This specific heat is not the same at all temperatures but is generally greater at high temperatures than it is at low. In common usage, specific heat is therefore given in one of three ways. First, true specific heat at some definite temperature; second, mean or average specific heat between some two extremes of temperature; third, specific heat expressed in a formula by means of which it may be calculated for any temperature within the range covered by the formula. The accompanying table of the true specific heats of certain of the more common metals at zero degrees centigrade shows the wide variations in this property.

SPECIFIC HEAT OF METALS AT 0° C.

Aluminum	0.2220*	Zinc	0.0906
Iron	0.11012	Silver	0.0555
Nickel	0.10836	Tin	0.0560
Copper	0.0939	Lead	0.02925

* J. W. Richards: "Metallurgical Calculations," 1, 60 seq. N. Y., 1906. McGraw-Hill.

In the table of specific heats of nickel, as given by Behn, it is stated that the specific heat of nickel at 186° below zero centigrade is 0.0572; at 79° below zero, it is 0.0888; at zero, it is 0.0934; and at 18° above zero it is 0.109. This shows that the specific heat increases as the temperature rises.

The formulas given by Pionchon[11] for the temperature coefficient of specific heat for nickel prepared by calcination of chemically purified oxalate and reduction by hydrogen are:

From 0° to 230° C., $0.10836 + 0.00004466t$.
230° to 400° C., $0.183493 + 0.000564t + 0.000001399998t^2$.
400° to 1150° C., $0.099 + 0.00006175t$.

The variations show allotropic modifications between 220° and 400° C.

Said to be pure nickel,[12] from 0° to 320° C., $0.1043 + 0.0000473t$.

To know the specific heat of nickel at 150° C. therefore, the formula is applied as follows:

$$t = 150° \text{ C.},$$

$$0.10836 + 0.00004466t = 0.10836 + (0.00004466 \times 150) = 0.11509.$$

The specific heat of nickel at 150° C. is, by this formula, 0.11509.

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[11] *Comp. Rend.* (1886) **103**, 1123.
[12] Naccari: *Zeit. Phys. Chem.* (1888) **2**, 439

TABLE 4.—*Specific Heat of Nickel*

References	Remarks	Temperature, Degrees C.	Specific Heat
		From	
Tilden: *Proc.* Roy. Soc. Lond. (1900) **66**, 244.	Using nickel very carefully prepared from nickel carbonyl and fused in hydrogen	Mean −182.4 to −78.4	0.0719
		Mean −78.4 to +15	0.0975
		Mean +15 to +100	0.1084
Tilden: *Phil. Trans.* **A194**, 233.	Same material as above.....	True at 182.5	0.0838
Behn: *Wied. Ann.* **66**, 237.....	98 per cent. nickel rolled.....	Mean −186 to +18	0.0857
		Mean −79 to +18	0.0983
Behn: *Ann. Phys.* [4] (1900) 1, 261.		Mean −186 to −79	0.0743
		Mean −79 to +18	0.0983
		Mean +18 to +100	0.109
		True at −186	0.0572
		True at −79	0.0888
		True at 0	0.0934
		True at +18	0.1053
Jaeger and Diesselhorst: Berl. Akad. der Wiss. Sits. (1899) **39**, 26.	Impure nickel containing Co 1.4; Fe 0.4; Mn 1.00; Cu 0.10.	True at 18	0.1063
		True at 100	0.1159

LATENT HEAT OF FUSION

Latent heat is the quantity of heat that must be communicated to or abstracted from a body in a certain state to change it to another state without altering its temperature. The following table shows the latent heat of fusion of certain metals:[13]

Aluminum	100	kilo calories per kilo
Iron	70	kilo calories per kilo
Nickel	68	kilo calories per kilo
Copper	44.3	kilo calories per kilo
Silver	24.35	kilo calories per kilo
Tin	13.82	kilo calories per kilo

LATENT HEAT OF CHANGE OF STATE

On heating nickel past the transformation point, 325° C. heat is absorbed by the metal in changing from one form to the other. Richards[14] gives this latent heat of change of state of nickel as 4.64 calories absorbed between 230° and 400° C. per kilo of nickel.

THERMAL CONDUCTIVITY

The thermal conductivity of nickel is low when compared with that of copper, as shown by the following:

Silver	1.096	Nickel	0.14
Copper	0.72	Tin	0.14
Aluminum	0.35	Lead	0.08[15]
Iron	0.17		

[13] Richards: "Metallurgical Calculations," 1, 58.

[14] *Op. cit.*, 67.

[15] H. O. Hofman: "General Metallurgy," 29. N. Y., 1913. McGraw-Hill.

Table 5 shows certain detailed data concerning this property:

TABLE 5.—*Thermal Conductivity of Nickel*

Reference	Remarks	Temperature, Degrees C.	Conductivity, C.G.S. Units
Baillie: *Trans.* Roy. Soc. Edin. (1897–98) **39**, 361.	Material contained Ni 97.22; Fe 0.75; Mn 1.68; Mg 0.28. Tested by Forbes' indirect method.	40	0.118
		50	0.121
		60	0.125
		70	0.130
		80	0.133
		90	0.135
		100	0.137
		110	0.138
		120	0.139
		130	0.139
		140	0.140
		150	0.142
	Tested by direct method.....	20 to	0.130
		250	0.136
Lees: *Phil. Trans.* (1908) **A208**, 381.....	Nickel 99 per cent.....	18	0.140
Jaeger and Dieselhorst: Wiss. Abh. Phys. Tech. Reichs 3, 1900, 269.	Ni 97.0; Co 1.4; Fe 0.4; Mn 1.00; C 0.1; Si 0.1.	18	0.1420
		−160	0.129

MAGNETIC PROPERTIES OF NICKEL

These peculiar properties of nickel are at present of greater academic than practical interest. They are, however, extremely suggestive and are here given in brief summary in order to show that while in some respects the magnetic properties of nickel are less than iron, in other respects they are greater. On the whole, these properties present a field for experiment that so far has been but little explored and which may prove of greater interest in the future developments of applied science. The cycle magnetization of nickel wire (0.068 cm. diameter and 25.4 cm. long) has been studied by Ewing and Cowan,[16] who give the following figures showing the intensity of magnetization I to the force H.

TABLE 6.—*Intensity of Magnetization of Nickel Wire (Annealed)*

Magnetising Force, H	Magnetic Intensity, I	Magnetic Susceptibility, K	Magnetising Force, H	Magnetic Intensity, I	Magnetic Susceptibility K
0	22		24.6	325	13.2
4	36		52.6	371	7.1
6.5	83	12.8	79.7	392	4.9
8.0	177	22.1	100.4	401	4.0
9.5	223	23.5	0.0	284	
10.9	251	23.0	−7.5	0	
12.3	273	22.2			

[16] *Phil. Trans.* (1888) **A179**, 327.

The last two figures in columns H and I show the residual magnetism and the coercive force. The greatest susceptibility (K = 23.5) at a force H of 9.5 corresponds to a permeability μ = 283. This may be compared with the curve given by Ewing,[17] for soft annealed iron wire. The maximum susceptibility K = 245 occurs at a force of H = 2.6 and the maximum permeability μ = 3080.

The saturation value of I in nickel, according to Ewing, is one-third or one-fourth of the saturation value in wrought iron. Nickel is extremely sensitive in its magnetic properties to stresses,[18] its susceptibility being greatly increased by compressive stresses and greatly diminished by tensile stresses. The maximum permeability μ of a sample of nickel under no load was about 225, while the permeability under a compressive stress of 6.8 kilos per sq. mm. was about 350. Tables 7 to 10 show the permeability of wrought iron and of nickel in a strong field. Under sufficiently strong magnetization forces the intensity of magnetization I reaches a constant or very nearly constant value in iron and nickel.

TABLE 7.—*Swedish Iron*

H	B	I	μ
1,490	22,650	1680	15.20
3,600	24,650	1680	6.85
6,070	27,130	1680	4.47
8,600	30,270	1720	3.52
18,310	38,960	1640	2.13
19,450	40,820	1700	2.10
19,880	41,140	1700	2.07

TABLE 8.—*Hard-drawn Nickel* (*Fe* 0.56)

H	B	I	μ
2,220	7,100	390	3.20
4,440	9,210	380	2.09
7,940	12,970	400	1.63
14,660	19,640	400	1.34
16,000	21,070	400	1.32

TABLE 9.—*Annealed Nickel* (*Fe* 0.75)

H	B	I	μ
3,450	9,850	510	2.86
6,420	12,860	510	2.00
8,630	15,260	530	1.77
11,220	17,200	480	1.53
12,780	19,310	520	1.51
13,020	19,800	540	1.52

TABLE 10.—*Nickel in Strong Fields*

H	B	I	μ
550	6,420	453	11.67
3,410	9,920	518	3.12
6,290	12,850	522	2.57
9,600	16,250	527	1.69
12,620	19,220	525	1.52

[17] "Magnetic Induction in Iron and Other Metals," 3d Ed., 82.

[18] Kelvin Reprint, 2, 382; Ewing and Cowan: *Phil. Trans.* (1888) A179, 325 and 335.

Du Bois[19] found that the limit of intensity of magnetization was 530 in nickel and 1630 in hard English cast steel. He gives the factors in Table 10 for best nickel wire hard drawn and said to contain 99 per cent. nickel.

The effect of increase in temperature on the magnetic properties of iron is well known. Wrought iron is highly susceptible to magnetic induction as long as the temperature does not exceed 775° C. Up to this point the effect of heating is to increase the susceptibility of iron, and at 775° C. the susceptibility is many times greater than when the iron was cold. But with further heating an extremely rapid loss of magnetic quality ensues and when the temperature has risen only 11° higher, to 786° C., the iron has become practically non-magnetic. Its permeability at 786 is only 1.1 whereas at 775 it is no less than 11,000.[20] In an impure specimen of nickel, Hopkinson found this change of magnetic quality occurred at 310° C.[21] This temperature marks the point at which a molecular change of state occurs. Rowland,[22] examining the susceptibility of nickel at 5° C. and at 230° C., found that at the higher temperature there was much more susceptibility to weak magnetic forces than at the lower temperature but less susceptibility to strong forces. The main points of difference in the magnetic behavior of nickel and iron, with respect to temperature, is that in nickel the effects of temperature, when the temperature is low, are more considerable than they are in iron, that in nickel the critical point is much lower and that the change from the magnetic to the non-magnetic state is much less abrupt.[23]

The effect of stress on the magnetic properties of nickel is much greater than on iron.[24] Nickel wire (0.068 cm. in diameter) tested under tension shows an enormous reduction in its susceptibility. With no load, the maximum susceptibility was 15; with a load of 2 kilos, the susceptibility was 8; and with 12 kilos, the resistance to magnetization became so great that the maximum of susceptibility was not reached with a magnetizing force of 100 C.G.S. The presence of tensile load reduced the residual magnetism even more than it reduces the total induced magnetism. On the other hand, compressive stresses greatly increase the susceptibility and retentiveness of nickel.[25] In testing a nickel rod under increasing compressive load, it was found that each addition of load produced a decided increase of susceptibility and caused an increasing fraction of the whole magnetism to remain as residual magnetism. With a maximum load 19.8 kilos per sq. mm., the induced magnetism I reached

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[19] *Phil. Mag.* [5] (1890) **29**, 293; Ewing: "Magnetic Induction in Iron," 162.
[20] Hopkinson: *Phil. Trans.* (1889) **A180**, 443: Ewing: *Op. cit.*, 176.
[21] *Proc.* Roy. Soc. Lond. (1888) **44**, 319.
[22] *Phil. Mag.* [4] (1874) **48**, 321; also Baur: *Wied. Ann.* (1880) **11**,
[23] Ewing: *Op. cit.*, 177.
[24] *Phil. Trans.* (1888) **A179**, 325 and 333; Ewing: *Op. cit.*, 199.
[25] *Phil. Trans.* **A179**, 333; Ewing: *Op. cit.*, 203.

a maximum of 450, with a magnetizing force H of 30, and the residual magnetism at this point was 430, or 96 per cent. of the maximum induced magnetism. The permeability μ of nickel is about 75 under no compressive load, while with a load of 19.8 kilos per square mm. it is about 360.

When nickel is subjected to a combined stress of twisting and tension, some very curious phenomena are noted. Nickel reverses its polarity under the combined influence of pull and twist while iron does not. The magnetism of nickel increases with twist instead of decreasing, as it does in iron. All these changes may be studied in full in the papers by Nagoaka,[26] Zehner[27] and others mentioned in the foot-notes. Ewing gives an admirable summary.

Iron expands under the influence of magnetizing forces and the elongation of the specimen increases as the magnetizing force increases, up to a certain maximum. With higher forces still the iron retracts. With nickel, however, there is retraction from the first.[28]

Electrical Resistivity of Nickel

On account of the various methods of production and the resulting variations in chemical composition, the electrical resistivity of nickel has been variously reported on by different observers. The average electrical resistivity of American malleable nickel of the grades described are as follows:

Material	Grade A	Grade C
Electrical resistivity	64 ohms per mil-ft. at 24° F.	80 ohms per mil-ft. at 24° F.
Temperature coefficient	0.0023 per degree F.	0.0023 per degree F.

[26] *Jnl. Coll. Sci. Imp. Univ.*, Japan (1888) **2**, 283-304; (1889) **3**, 189; (1890) **4**, 335.

[27] *Wied. Ann.* (1889) **38**, 68; (1890) **41**, 210.

[28] Barrett: *Nature* (1882) **26**, 855.
Bidwell: *Proc.* Roy. Soc., Lond. (1886) **40**, 109.
Phil. Trans. (1888) **A179**, 205.
Proc. Roy. Soc. Lond. (1890) **47**, 469.
Ewing: *Op. cit.*, 249.
H. Tomlinson: *Phil. Mag.* [5] **25**, 372–379; *Jnl.* Chem. Soc. (1888) **54**, 892.
Ewing: *Phil. Trans.* (1885) **176**, pt. 2, 523.
Ewing and Cowan: *Chem. News*, (1888) **57**, 203.
Curie: *Compt. Rend.* (1894) **118**, 1134.
Leick: *Wied. Ann.* (1896) **58**, 708.
Beattie: *Phil. Mag.* (1901) **1**, 643.
Shaw and Laws: *Electrician* (1901) **46**, 739.
Nagaoka and Honda: *Phil. Mag.* [6] (1902) **4**, 71.
Gray and Wood: *Proc.* Roy. Soc. Lond., (1902) **70**, 294.
Knott: *Trans.* Roy. Soc. Edin. [3] (1902) **40**, 535.
Honda and Shimezu: *Phil. Mag.* [6] (1902) **4**, 343.
Knott and Ross: *Proc.* Roy. Soc. Edin. (1902) **24**; (1903) **25**, 501.
Nagaoka and Kusakabe: Mach. and Phys. Soc. Tokyo (1901–03) 97.
Russell: *Proc.* Roy. Soc. Edin. (1903–05) **25**, 309; (1908) **29**, 38–56
Knott: *Proc.* Roy. Soc. Edin. (1903) **25**, 292–294.

The results of other specific investigations follow:

Matthiessen and Vogt, in 1863, working on supposedly pure nickel wires determined the resistance of these wires in comparison with hard-drawn copper and silver.[29] The comparison showed that if hard-drawn silver had a conductivity of 100, hard-drawn copper had a conductivity 99.75 and nickel had a conductivity of 13.106. From these figures, it was calculated, by Fleming, that the resistance per centimeter cube of nickel was 12,357 C.G.S. units. This would be 12,357 microhms per centimeter cube.

In 1899, Hadfield published his paper on alloys of iron and nickel.[30] In the discussion of this paper Dr. Fleming stated that he had, in conjunction with Prof. Dewar, made experiments on the resistance of nickel at low temperatures. He used a thin tube of nickel produced by the Mond process. As the metal was so brittle that it could not be drawn into wire and as he did not wish to endanger the purity of the sample by remelting it, he cut it into a spiral and determined the relative resistance of this spiral at various temperatures. The spiral was not of uniform cross-section and the only way he could reduce his figures to standard units was to adopt Matthiessen's figure of 12,357 C.G.S. units at zero. Hence the published figures given by Fleming[31] are not to be taken as corroborating Matthiessen's determination. Fleming simply took Matthiessen's figures as correct. Fleming himself states[32] that in experiments on pure electrolytic nickel he found a specific resistance of 6935 C.G.S. units (6.935 microhms) per centimeter cube. This is only about one-half the resistance given by Matthiessen.

Campbell[33] reports experiments on two samples, the analysis of which is not given. A was procured in Germany in 1901, B was bought in the United States about 1895; it was presumed that A was the purer. The resistivity of A was 8 microhms and that of B 12 microhms per centimeter cube. Jaeger and Desselhorst[34] give their determinations on an impure nickel containing 1.4 per cent. cobalt, 0.4 per cent. iron, 1.00 per cent. manganese, and 0.1 per cent. copper as 8.50 microhms per centimeter cube at 18° C. and 6.37 at 100° C.

Harrison[35] gives 10.288 as the resistance of nickel. Copaux[36] working on nickel of exceptional purity made from chemically purified oxalate reduced by hydrogen to a metallic sponge, hydraulically compressed

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[29] *Ann. Pogg.* (1863) **117**, 431–434; *Phil. Trans.* (1863) **153**, 383.
[30] *Proc.* Inst. Civ. Engrs. (1898–99) **138**, 4.
[31] *Phil. Mag.* (1893) **36**, 271–299.
[32] *Proc.* Roy. Soc. Lond. (1899–1900) **66**, 50–58.
[33] *Elec. Rev.* (1901) **48**, 1014.
[34] Berlin Akad. der Wiss. Sitz. (1899) **38**, 726.
[35] *Phil. Mag.* (1902) **6**, 191.
[36] *Ann. Chim. et Phys.* [8] (1905) **6**, 508–574.

and annealed in hydrogen, found a resistivity of 6.4 microhm per centimeter cube. Pécheux[37] took four samples of nickel and determined their resistance. The figures for these at zero are:

Copper	Iron	Cobalt	Carbon and Silicon	Resistivity in Microhm, Cubic Centimeters
0.20	Trace	0.15	0.0	9
0.80	Trace	Trace	0.20	10.24
0.40	0.60	0.10	0.15	14.25
Trace	1.50	0.50	0.10	13.25

Kalmus and Harper[38] found an analogous condition of variations in their determinations of resistance of cobalt. Commercial cobalt unannealed was found to have nearly three times the resistance of chemically purified cobalt. When the samples were annealed this difference largely disappeared but the authors state that the electrical resistance is tremendously influenced by impurities or by absorbed or occluded gases. The same is undoubtedly true of nickel, which accounts for the large variations found by various observers. It will, however, be noticed that determinations made by two reliable observers on exceedingly pure nickel give 6.396 microhms (Fleming) and 6.4 microhms (Copaux). These may be taken as the best data at present available on the purest specimens.

Coefficient of Expansion of Nickel

In Table 11 are given a number of the determinations of the coefficient of expansion of nickel. Its commercial value lies in its near relation to that of steel, thus permitting the two metals to be used in conjunction under conditions of varying temperature change without distortion or relative changes of size and shape.

Occlusion of Gases

Nickel, at a constant temperature, absorbs hydrogen in proportion to the square root of the pressure used; and, at a constant pressure, the solubility increases with the temperature and shows a sudden increase at the melting point of the metals.[39]

Oxygen is absorbed by molten nickel either by direct occlusion or by solution of nickel oxide in the molten metal in much the same way that copper dissolves copper oxide. For this reason both copper and nickel are weakened by remelting unless some steps are taken to regulate the oxygen thus taken up. Manganese, aluminum, and magnesium have the power of removing oxygen; magnesium is most commonly used. A stick of magnesium is thrust by a tongs into a pot of melted nickel and

[37] *La Lumière Électrique* (1910) **10**, 232–239.
[38] *Jnl.* Ind. and Eng. Chem. (1915) **7**.
[39] Ellis: "Hydrogenation of Oils." Van Nostrand, 1914.

TABLE 11.—*Coefficient of Expansion of Nickel*

Reference	Remarks	Formula for Coefficient at $t°$ C.
Vogt: *Wied. Ann. Phys. Chim.* (1893) **49**, 704		$13.15+0.0413\ (t-30)\times10^{-6}$
Guillaume: *L'Éclairage Électrique* (1898) **16**, 287	Pure nickel of commerce annealed 0° to 30° C.	$(12.666+0.00542t)\times10^{-6}$
Guillaume: *Arch. des. Sci. Phys. et Nat.* [4] (1898) **5**, 261	Ferronickel Co. nickel 1891	$(12.655+0.00550t)\times10^{-6}$
	Ferronickel Co. nickel	$(12.523+0.00661t)\times10^{-6}$
	Baase and Selve nickel	$(12.491+0.00702t)\times10^{-6}$
	Ferronickel Co. nickel 1895	$(12.493+0.00790t)\times10^{-}$
	Ferronickel Co. nickel	$(12.551+0.00542t)\times10^{-6}$
Tutton: *Proc.* Roy. Soc. Lond. (1899) **65**, 308	Pure nickel from nickel carbonyl	$(1248+0.74t)\times10^{-6}$
Holborn and Day: *Ann. Phys.* [4] (1901) **4**, 104	Linear expansion per unit of absolute length at 0°. Formula holds good for temperatures above 375° C.	$(13460t+3.315t^2)\times10^{-9}$
Harrison: *Phil. Mag.* 6] (1904) **7**, 626	Pure nickel wire. Formula holds good for temperatures up to 300° C	$(1280+0.75t+0.0035t^2)\times10^{-9}$
	0– 50° C.	0.0000128
	50–100	0.0000136
	150–200	0.0000151
	250–300	0.0000174
	300–350	0.0000191
	350–365	0.0000205
	380–400	0.0000191
	400–450	0.0000189
	450–500	0.0000192
	500–550	0.0000190
Guillaume: Geneve, 4th Period. *Arch. Phys. Nat.*, **5**, 255, 305	Nickel from Société du Ferro Nickel 1891	$(12.655+0.00550t)10^{-6}$
	Nickel from Société Française du Nickel 1891	$(12.523+0.00661t)10^{-6}$
	Nickel from Baase and Selve	$(12.491+0.00702t)10^{-6}$
	Nickel from Société du Ferro Nickel 1895	$(12.493+0.00790t)10^{-6}$
	Nickel from Société Française du Nickel 1895	$(12.551+0.00542t)10^{-6}$
	Containing about 98 per cent. nickel	$(12.514+0.00674t)10^{-6}$

stirred briskly around. About 1½ oz. of magnesium will deoxidize 100 lb. of nickel. The metal then cast into ingots can be rolled or forged. A larger amount of magnesium will do positive harm as, for some reason, it makes the melted metal thick and sluggish to pour.

TABLE 12.—*Occlusion of Gases*

Reference	Remarks	Volumes of Hydrogen Occluded by Unit Volume of Nickel
Raoult: *Compt. Rend.* (1869) **69**, 826...	Porous nickel cubes, treated electrolytically.....	165.0
Troost and Hautefeuille: *Compt. Rend.* (1875) **80**, 788.	Pure ingot heated to redness in hydrogen, cooled in hydrogen.....	0.20
	Sheets electrolytic treatment.....	40.0
	Sheets heated in hydrogen.....	16.0
	Sheets electrolytic treatment.....	10.0
	Powder by reduction of oxide in hydrogen.....	100.0
Bellati and Lusanna: Roy. Inst. Veneti. (1888) **6**.....	Impure wire, electrolytic treatment.....	100.0
Neumann and Streints: "Monatsheft fur Chemie," 657. 1891.....	Powder from oxalate heated in hydrogen.....	17.5
Barter: *Am. Chem. Jnl.* (1899) **22**, 360.	Spongy metal freed from every impurity, reduced from oxide by hydrogen, treated by various methods of heating and cooling.....	3 to 10.7
Mayer and Altmayer: *Ber. Deut. Chem. Gesell.* (1908) **41**, 3062.	Nickel powder reduced from oxide by hydrogen, Pressure, 360 mm. at 360° C.....	50.5
	Pressure, 440 mm. at 560° C.....	50.5

TABLE 13.—*Occlusion of Gases*

Reference	Remarks	Temperature, Degrees C.	Milligrams Hydrogen Dissolved by 100 Gm. Nickel
Sieverts and Krumbhaar: *Ber. Deut. Chem. Gesell.* (1910) **43**, 893. Zeit. Phys. Chem. **77**, 591. *Tabelles Annuelles* (1911), 431.	Nickel wire Ver. Deut. Werke 98.5 per cent. nickel. Nickel wire Langbeim. Pfannhausen. 99.2 per cent. Nickel heated in hydrogen at	212	0.16
		314	0.22
		419	0.30
		520	0.39
		620	0.52
		721	0.62
		822	0.72
		923	0.86
		1023	0.98
		1123	1.148
		1225	1.333
		1265	1.359
		1300	1.320
		1327	1.508
		1345	1.487
		1400	1.539
		1451	Nickel melts
		1465	3.50
		1500	3.59 3.63 3.75
		1600	3.86 3.88

Decoloring Power

Nickel has, of all metals, the strongest decoloring power on copper. Even 1 or 2 per cent. makes copper very perceptibly paler and an alloy of 25 per cent. nickel and 75 per cent. copper is almost as white as pure nickel. Table 14, from Brandt's "Metallic Alloys," compares the decoloring power of nickel with that of tin and zinc.

Table 14.—*Decoloring Power of Nickel, Tin, and Zinc when Alloyed with Copper*

Copper-nickel Alloys		Copper-tin Alloys		Copper-zinc Alloys	
Per Cent. Nickel	Color	Per Cent. Tin	Color	Per Cent. Zinc	Color
5	Much paler than pure copper	5	Red yellow, gold like	5	Red almost copper color
10	Light copper red	10	Reddish gray yellow	10	Yellowish, red brownish
15	Very pale red	16	Reddish yellow	16	Red yellow
20	White with pink cast	20	Reddish gray	20	Reddish yellow
		22	Yellow gray	22	Reddish yellow
25	Nearly white	25	Reddish white	25	Pale yellow
				27	Yellow
30	Silver white	30	White	30	Yellow

Effect of Chemical Composition on Properties of Nickel

Like iron, nickel may contain carbon, silicon, sulfur, and other elements that modify its properties. As in iron and steel, certain substances may be purposely introduced into the nickel for the beneficial effects they produce, while certain other elements, such as sulfur, are an accident of manufacture and are avoided as deleterious.

Carbon.—Nickel, like iron, absorbs carbon by cementation. Samples packed in a pipe with carbon and heated for 10 hr. at 700° to 900° C. and allowed to cool slowly, gave the following results.

	Carbon Contents	
	Before Cementation	After Cementation
Electrolytic nickel	0.15	0.33
Malleable nickel	0.18	0.43

Nickel melted in a cupola furnace absorbs carbon almost as does pig iron and samples of such pig nickel may contain 2 or 3 per cent. of carbon, most of which is graphite.

Ruff and Martin[40] found that the solubility of carbon in nickel reaches a maximum of 6.42 per cent. at 2100° C., above which temperature the solubility decreases slightly. The composition corresponds to Ni_3C, which appears under the microscope as a brownish material very difficult

[40] *Metallurgie* (1912) **9**, 143; *Sci. Abs.* (1912) **15A**, Abs. 954.

to etch. This substance decomposes much more rapidly than cementite (Fe_3C with 6.6 per cent. carbon) on cooling; the result is that by far the greater part of the carbon even in quenched nickel alloys occurs as graphite. The system according to these investigators is quite analogous to the Fe_3C system.

Ruff and Gersten[41] found that the molecular heat of formation of Ni_3C is $-$ 394 $\pm$ 10 cal. while that of Fe_3C is $-$ 15.3 $\pm$ 0.2 cal.

The presence of carbon lowers the melting point of nickel. This has been carefully investigated by Friedrich and Leroux,[42] who have determined the melting point of nickel containing up to 2.6 per cent. carbon, but point out that the results do not represent complete equilibrium as the alloys contained 0.2 to 0.6 per cent. iron and, on account of the instability of the high carbon alloys, rapid cooling was resorted to. They find that carbon lowers the melting point of nickel (1451° C.) until a eutectic point is reached between 2 and 2.5 per cent. carbon. The eutectic line is situated between the temperature limits 1307° and 1318° C. Microscopic examination confirms the thermal results. A 2.6 per cent. carbon alloy shows clearly the presence of the carbon carrier, probably a carbide of nickel. The quenched alloys have the same properties as those slowly cooled, which confirms the absence of critical points in the cooling curves. The effect of carbon on the melting point of nickel is given by Friedrich and Leroux as follows:

Nickel	Iron	Carbon	Temperature of Beginning of Crystallisation, Degrees C.
99.9			1451
98.6	0.6	0.7	1409
99.0	0.21	0.8	1402
98.8	0.21	1.0	1361
98.3	0.21	1.5	1349
97.8	0.21	2.0	1328
97.2	0.21	2.6	1328

Of all of the elements commonly added to malleable nickel the influence of carbon is the greatest. It adds to the strength and hardness of all grades of malleable nickel. It makes the metal work better hot, especially, during the breaking down or cogging operation but greatly increases the difficulty of cold working. Its effect in this case is twofold, in that the higher carbon nickel, when fully annealed, is harder than the low carbon; it also hardens faster under the influence of cold working. At about 0.40 per cent. carbon, the separation of graphitic carbon begins to take place and this separation is accompanied by a progressive loss of malleability.

Although the alloys of nickel and carbon resemble those of iron and carbon in the shape of their freezing-point diagrams and in the formation of an analogous carbide, the nickel-carbon alloys do not undergo the

[41] *Ber. Deut. Chem. Gesell.* (1913) **46**, 400; *Chem. News* (1913) **107**.
[42] *Metallurgie* (1910) **7**, 10–13; *Sci. Abs.* (1910) **13A**, Abs. 755.

TABLE 15.—*Effect of Carbon on Nickel Hot-rolled Rods; Normal Samples are as Rolled and Unannealed*

No.	Sample, Number and Analysis						Brinell Hardness		Per Cent. Elongation		Yield Point, Lbs. per Sq. In.		Tensile Strength, Lbs. per Sq. In.	
	C	Fe	S	Si	Mn	Ni	Normal	Annealed	Normal	Annealed	Normal	Annealed	Normal	Annealed
E 154	0.063	0.28	0.017	0.094	0.22	99.27	107	89	37.1	44.5	21,375	23,500	68,875	67,500
N 16	0.08	0.63	0.026	0.04	.....	99.08	102	92	46.0	46.0	21,875	23,500	68,750	66,500
N 20	0.09	0.64	0.024	0.09	0.15	98.91	109	92	44.2	46.0	23,750	22,000	73,125	70,000
E 153	0.26	0.56	0.016	0.13	0.48	98.54	135	99	37.6	42.0	34,375	29,500	93,625	87,000

great number of transformations in the solid state that make steel such a varied and valuable product. As far as is now known, the presence of carbon introduces no transformations. Apart from annealing, nickel is not susceptible to heat treatment. As noted before, it has a transformation point at about 330° C., dividing the magnetic from the non-magnetic states, but this transformation is not accompanied by any structural change and has apparently no further bearing on the properties of the metal.

In Table 15 are given four examples of the influence of carbon on the properties of nickel. It is generally stated in metallurgical works that carbon is harmful to malleable nickel and that its presence should be avoided. This is not the case. The presence of *graphitic* carbon is undoubtedly harmful. Apart from the use of a vacuum furnace, we know of no manner in which malleable nickel ingots, free from carbon, can be produced. While undoubtedly the cold malleability is higher with decreasing carbon content, the presence of carbon in increasing amounts improves the quality of the ingot and adds to its hot malleability and also furnishes the most satisfactory means of varying the hardness and strength of the product and so adapting it to a variety of uses.

Manganese.—Manganese is generally absent from non-malleable, commercial nickel. In malleable nickel it is almost always present, being added intentionally, and imparts very beneficial properties. From a manufacturing standpoint, manganese is chiefly useful in increasing the fluidity of the molten nickel and thus rendering easier the production of good surfaced ingots. It also renders the metal

less tender just after freezing and thus aids in the production of ingots free from pulls or hot cracks. It also renders the ingot less tender during the first hot rolling operation. These results may be accomplished by comparatively small additions. Added in larger amounts, it increases the resistance of nickel to oxidation and renders it less susceptible to the action of sulfur in the fuels used in hot rolling. Manganese, up to 2 per cent., has little effect on the hardness or the tensile properties of nickel; the effect of higher percentages has not been studied in detail. It is known, however, that alloys containing up to 10 per cent. of manganese can be hot-rolled successfully. Manganese decreases the electrical conductivity of nickel.

Iron.—In commercial nickel, iron is always present as an incident of manufacture. It comes either from the imperfect removal of iron present in the original ore or from the tools used in the roasting and refining furnaces. The amount present is usually less than 1 per cent., in which case it has practically no influence on the properties of the metal.

Silicon.—Silicon is present in small amounts in all furnace-refined nickel. It is usually under 0.25 per cent. and has comparatively little effect in such amounts. Larger amounts increase both the hardness and the strength with an accompanying loss of ductility. Malleability at a red heat is also diminished and finally destroyed.

Cobalt.—Cobalt is a common impurity in nickel produced from Canadian ores. It is commonly determined with the nickel in chemical analysis and is considered as part of the nickel content. As far as is known, this is true of nickel containing up to 1 per cent. cobalt, which constitutes the bulk of American production.

Sulfur.—Sulfur is also an invariable constituent of all nickel except electrolytic nickel. It should be held at as low a point as possible, since it decreases ductility both hot and cold.

Tensile Properties of Nickel

The tensile properties of nickel are a function both of the treatment and of the quantity and kind of impurity present; and in all commercial malleable nickel carbon is the element of greatest weight. In the following table are given the ranges that may be normally expected in commercial American malleable nickel in the fully annealed and hard cold-rolled states:

	Annealed	Cold Rolled
Yield point, lb. per sq. in.....	20,000 to 30,000	90,000 to 110,000
Tensile strength, per sq. in.....	60,000 to 90,000	100,000 to 120,000
Elongation in 2 in., per cent.....	40 to 50	15 to 20
Reduction of area, per cent	45 to 55	40 to 50

Hardness of Nickel

The hardness of nickel and the influence of varying chemical and physical conditions is set forth in Table 16. Attention is called to the preponderating influence of carbon on this property.

Table 16.—*Hardness of Nickel*

Chemical Composition

Heat No.	E154	N16	N20	E153
Carbon, per cent	0.06	0.08	0.09	0.26
Manganese, per cent	0.22	0.00	0.15	0.48
Iron, per cent	0.28	0.63	0.64	0.56
Silicon, per cent	0.094	0.04	0.09	0.13
Sulfur, per cent	0.017	0.026	0.024	0.017
Nickel, per cent	99.27	99.08	98.91	98.54

Comparison of Effect of Hot or Cold Rolling

Annealed at 900° and slowly cooled	89	92	92	99
Hot rolled to a reduction of 75 per cent. thickness	99	103	112	137
Cold rolled to reduction of 75 per cent. thickness	228	223	235	332

Effect of Progressive Cold Rolling

	Brinell	Shore	Brinell	Shore	Brinell	Shore	Brinell	Shore
Hot-rolled bar before cold rolling	99	13	103	15	112	13	137	14
Same bar cold rolled until reduced 25 per cent. of its thickness	170	28	170	28	187	28	241	34
Same bar cold rolled until reduced 50 per cent. of its thickness	196	28	212	29	217	33	293	39
Same bar cold rolled until reduced 66 per cent. of its thickness	217	33	217	33	235	35	302	44
Same bar cold rolled until reduced 75 per cent. of its thickness	228	35	223	35	235	35	332	40
Same bar heated to 900° C. and slowly cooled in furnace	89	9	92	9	92	9	99	11
Specimen number, see analysis above	E 154		N 16		N 20		E 153	

Welding Properties

In the ordinary sense, nickel cannot be welded. By this is meant that it cannot be heated in an ordinary blacksmith's forge and hammered to a solid weld, as can be done with wrought iron. This is due solely to our lack of knowledge of a proper flux that will dissolve and remove the oxide of nickel produced by heating. Under suitable conditions, in which both the heating and working are conducted in reducing atmospheres, nickel welds readily. This is shown by the fact that shaped forms of nickel oxide reduced by carbon at temperatures below the melting point of nickel unite to form the "cubes" or "rondelles" of commerce.

Nickel can be welded by means of the oxyacetylene flame, by an

electric spot-welding process, or by any of the butt-welding processes where the two pieces form electrodes and are pushed together so as to extrude the oxide from the weld. In this way, nickel wire is welded to iron wire to form tips, or points, for spark plugs.

Shrinkage on Casting

The patternmakers shrinkage, or change in size taking place in nickel between the customary pouring temperature and room temperatures is approximately ¼ in. (0.244 in.) to the foot.

Malleable Nickel

Most of the nickel of commerce is non-malleable; and since it is commonly used for the production of nickel alloys, this property is neither essential nor desirable. For certain purposes, such as the making of rods, sheets, wire, etc., malleability is essential and is imparted by the addition of 0.1 per cent. of metallic magnesium to the melted metal just before pouring it into the molds. It is essential that this magnesium be thrust rapidly under the surface of the metal and thoroughly stirred in, otherwise it will ignite and burn on the surface and the effect be lost. It should not be added in the furnace or thrown into the ladle before tapping. The effect of this small addition of magnesium is remarkable. Cast without it, nickel is weak, malleable neither hot nor cold, while the cast section is generally honeycombed with blowholes. Cast with it, the nickel is sound, homogeneous, strong, and capable of being worked either in the hot or cold state. With the removal of the blowholes comes the setting up of a pipe, which must be taken care of by the use of proper risers and of properly designed molds. In this malleable condition, it can be forged, rolled, cast, drawn into wire, spun, or otherwise worked into any of the various fabricated forms. In all manufacture of malleable nickel, the influence of carbon must be kept in mind and the metal must be furnaced in such a manner as to give the proper carbon content and also either exclude oxygen or reduce any oxygen absorbed by the bath.

Hot Working.—In the hot working of nickel, both the temperature and the condition of the flame used should be subject to careful control. For rolling, the preferable temperature is 1200° C. and the ingots should not be subjected to any temperatures much in excess of this as a condition of red shortness is reached at some point between the above temperature and 1300° C. The flame used should be as nearly neutral as possible and low sulfur fuel (oil) is essential to successful heating.

For hot rolling bars and rods of the usual cross-sections, the same design of rolls as is used for steel may be employed with success. Pure nickel and nickel alloys of high nickel content are very easily "guide marked" when hot; this point should be given careful attention.

Annealing and Pickling of Nickel

The annealing of nickel may be considered purely from the standpoint of relieving the strains set up by cold work, *i.e.*, any work below the annealing temperature. In the regular grades of commercial nickel, annealing begins at about 750° C. and the full softness is obtained at 900° C.; the degree of softness obtained is independent of the speed of cooling. It is essential that the metal be held at the annealing temperature long enough for the metal to come thoroughly to heat.

After a thorough study of this matter, both on laboratory samples and on commercial quantities in the course of manufacture, we wish to strongly urge the necessity of using 900° C. for the commercial annealing temperature and the importance of making sure that this temperature is attained and maintained for a sufficient period to give full softness.

Whenever commercially possible, all nickel should be annealed in tight boxes so as to prevent the formation of oxide and in order that any oxide present may be reduced by the creation of a reducing atmosphere in the box either by the presence of a small amount of charcoal or the admission of some reducing gas. When the annealing is done in this manner, no pickling is necessary; on account of the difficulty and expense, pickling should only be adopted as a last resort. If pickling cannot be avoided, it may be done by the use of sulfuric acid together with some oxidizing agent, such as ferric sulfate or chromic acid, at temperatures around 60° to 70° C. But at best it is a tedious and expensive operation.

DISCUSSION

William B. Price* and Philip Davidson,† Waterbury, Conn. (written discussion).—A few months ago we became interested in determining the properties of pure nickel as a metal for certain uses and arranged, in coöperation with the International Nickel Co., a series of tests on cold-rolled so-called pure nickel and both longitudinal and transverse specimens annealed at 100° intervals from 250° to 1050° C. Since our tests confirmed, in a general way, the observation put forth by Messrs. Browne and Thompson, they are given at this time.

A bar of hot-rolled nickel about 9 in. (23 cm.) wide and ½ in. (12.7 mm.) thick made by the International Nickel Co. of grade A stock, analyzing nickel plus cobalt 98.48 per cent., iron 0.67 per cent., manganese 0.27 per cent., carbon 0.07 per cent., silicon 0.162 per cent., sulfur 0.033 per cent., and copper 0.22 per cent., was cold-rolled down to a final thickness of 0.134 in., making a 73.2 per cent. reduction by rolling. Test specimens, 9 by 1 in., cut parallel (marked longitudinal) and normal

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†Metallurgist, Scoville Mfg. Co.

(marked transverse) to the direction of rolling were milled to give a test section $2\frac{5}{8}$ in. long by 0.5 in. wide. Three specimens each, longitudinal and transverse, were annealed at one time in a nichrome-ribbon-wound tube furnace. The temperatures were taken with a Pt-PtRh thermocouple in conjunction with an Engelhard millivoltmeter. An annealing period of $\frac{1}{2}$ hr. plus 25 min. preheating was used in all cases. Scleroscopic and Brinell hardness tests and static tensile tests were made on the rolled and annealed specimens. The tensile tests are shown in graphic form in Fig. 7. The Brinell and scleroscopic values are given herewith.

Treatment of Specimens	Brinell Number		Scleroscope	
	500 Kg.	3000 Kg.	Universal Hammer	Magnified Hammer
Cold rolled $\frac{1}{2}$ in. to 0.134 in.		235	37.0	71.0
250° C.		262	37.0	68.5
350° C.		255	36.7	70.5
450° C.		248	35.0	67.0
550° C.		228	32.0	60.0
650° C.	136	166	20.0	43.0
750° C.	74	112	9.5	20.5
850° C.	67	105	8.0	16.5
950° C.	63	101	7.0	15.0
1050° C.	61	101	6.5	14.5

Microstructure.—The micrographs, Figs. 1 to 6, show that, structurally, nickel behaves in practically the same way as a copper-zinc or copper-tin alpha solid solution, crystal twinning being much in evidence in material annealed after cold working As shown in Fig. 1, the hot-rolled material has been finished at a high enough temperature to leave the crystals in an equiaxed condition. Rolling deforms the grain and produces etch bands, as shown in Fig. 2.

The temperature of recrystallization of hard-rolled nickel sheet is some 300° C. higher than that of hard-rolled alpha brass. No visible recrystallization, as seen under moderate magnification, is noted until a temperature of 650° C. is attained. At 750° C. complete recrystallization takes place, as shown in Fig. 4; beyond this the grain size increases somewhat with the rise in annealing temperature.

Tensile Tests.—The results of tensile tests are shown graphically in Fig. 7. The first decided softening takes place at 650° C. and equilibrium conditions are nearly attained at 750° C. Beyond 750° C., the softening is very gradual. The longitudinal and transverse annealed specimens appear to behave very much the same in the case of all values except those

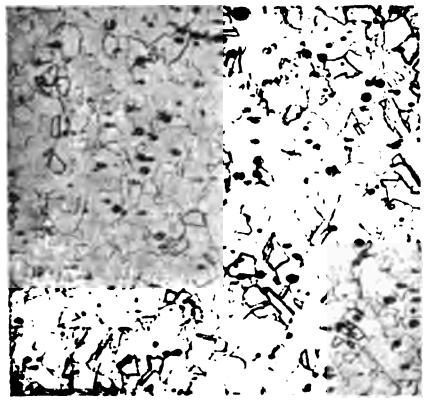


FIG. 1.—HOT-ROLLED BAR ON 0.5 IN. AS RECEIVED.

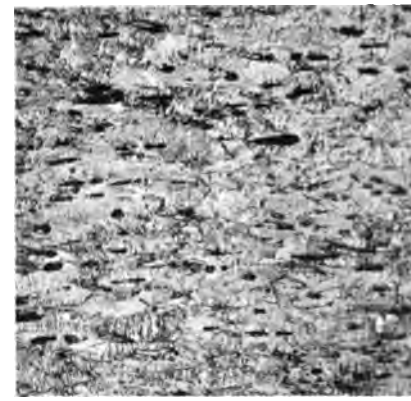


FIG. 2.—COLD-ROLLED FROM 0.500 IN. TO 0.134 IN.

FIG. 3.—SAME AS FIG. 2, ANNEALED AT 650° C.

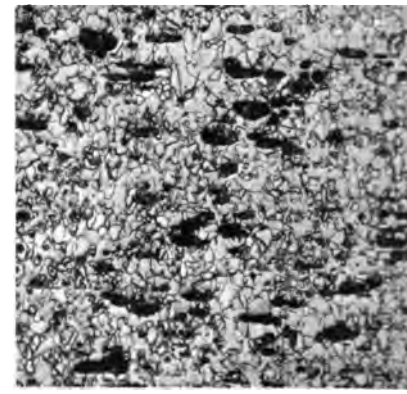


FIG. 4.—SAME AS FIG. 2, ANNEALED AT 750° C.

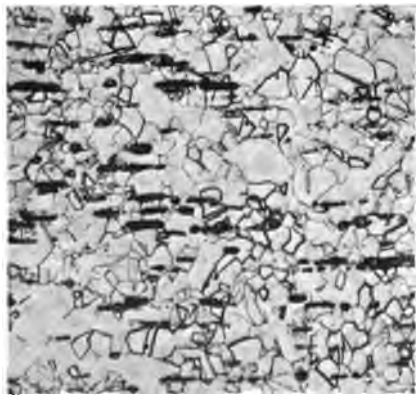


FIG. 5.—SAME AS FIG. 2, ANNEALED AT 850° C. ETCH: HNO_3 IN ALCOHOL. × 75.

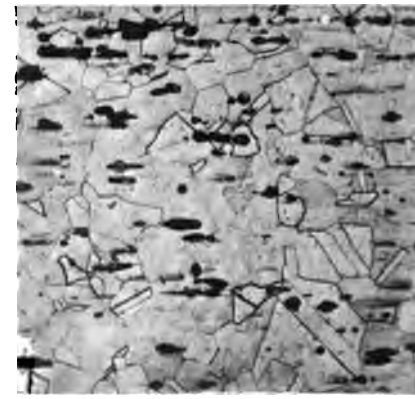


FIG. 6.—SAME AS FIG. 2, ANNEALED AT 1050° C.

representing reduction of area. Here the longitudinal values are higher than the transverse values by approximately 8 per cent. In the case of the hard-rolled specimens, the transverse specimens have a tensile strength some 10,000 lb. greater than the longitudinal.

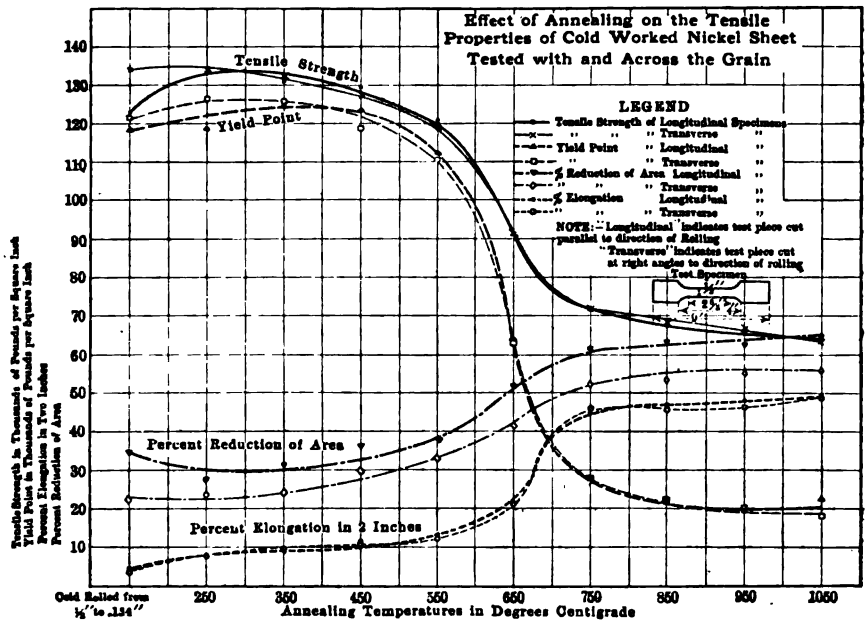


FIG. 7.

J. L. JONES,* Pittsburgh, Pa.—If a nickel anode is cast under commercial conditions, will it contain nickel oxide? Will the nickel oxide affect the rate of corrosion in a double sulfate solution; or will the nickel oxide dissolve in a double sulfate solution? I would also like to ask whether a 98 per cent. pure nickel anode will corrode as fast as a 96 per cent. nickel anode; whether electrolytic nickel will corrode less rapidly than nickel containing a small amount of carbon; and whether the materials sometimes used in coating molds for casting nickel anodes will affect the rate of corrosion of the anode? In other words, whether an electrically non-conducting coating is likely to be present that will prevent the nickel anode from corroding rapidly.

JOHN F. THOMPSON.—The nickel oxide will not dissolve in the double sulfate solution, as far as we know. We do not make the ordinary nickel anode of commerce, but we supply nickel to the nickel anode makers. Those makers almost invariably buy a high-carbon nickel shot, ranging around 0.45 per cent. carbon. In their process, they even further car-

* Metallurgist, Westinghouse Elec. & Mfg. Co.

burize it so as to get nickel that will melt easily and be fluid enough to fill the mold, so that the ordinary cast anode on the market is unquestionably oxide free. The only time that such an anode will have oxide will be through an error in melting. Some cupola makers of anodes have had trouble with oxidation, but as a rule the anodes are thoroughly carburized; so much so that they probably carry a couple of per cent. of carbon of which around 1.6 per cent. is graphite.

It is supposed by the anode makers that the anode containing carbon dissolves more readily than the carbon-free anode. This belief, I think, is pretty well supported.

With regard to the facing, I don't know; but this fact may be of interest to you: very often the surface of nickel shot when used in a basket anode will not dissolve so that the shot does not go into solution readily until a small hole is started through the skin, and then the metal inside of the shot will leak out and leave the outside skin.

J. L. JONES.—Is its microstructure different from the rest?

J. F. THOMPSON.—I do not know; I do not know what causes it.

J. L. JONES.—Do you think a similar condition would prevail in a mold that was very cold in comparison with nickel cast in a mold that was hot; would there be a difference in microstructure, possibly?

J. F. THOMPSON.—I think so. This fact I ran across only about 10 days ago, and I do not know the reason for it.

R. S. MACPHERRAN.—Was there any oxide outside of those shots; was there anything that would stop the solution?

J. F. THOMPSON.—No, the shot was perfectly bright and was made by swinging a spout over a big tank of cold water, so that the shot had a short fall. The surface appearance of the shot was perfectly white, even in the case of this shot where the internal erosions took place.

Mr. Jones asked about the electrolytic nickel. As far as we know, there is no difficulty in using electrolytic nickel as an anode for plating. Some people use it for that purpose.

W. H. BASSETT,* Waterbury, Conn.—Nickel cathodes when used as anodes in plating solutions do not dissolve as rapidly as ordinary cast anodes. When cathodes are used as anodes the nickel solutions become impoverished. It was impossible to make nickel cathodes give results equal to those obtained with cast anodes and it was found, upon investigation, that the trouble was due to the solutions becoming impoverished

* Technical Superintendent and Metallurgist, American Brass Co.

in nickel. Malleable nickel will act in exactly the same way, and the solution of malleable nickel anodes was found to be very much slower than that of cathode nickel when used as anodes.

J. F. THOMPSON.—I am interested in that statement. In foreign practice, they use a great deal of rolled malleable nickel. I don't know how they get it dissolved, but they say that for the last 10 years there has been quite a demand over there for rolled anodes.

W. B. PRICE, Waterbury, Conn.—The old method was to use double nickel salts; then, when using single nickel salts with the rolled nickel anodes they also introduce into the electrolyte nickel chloride, which seems to produce an active corrosion of the anodes, which doesn't take place in the old double nickel salts solution.

Physical Properties of Certain Lead-zinc Bronzes

BY HOMER F. STALEY,* B. A., AND C. P. KARR,† PH. B., WASHINGTON, D. C.

(Philadelphia Meeting, September, 1919)

THE casting alloy 88 copper, 10 tin, 2 zinc, commonly known in England as Admiralty metal and in this country as Government bronze, gun metal, or Naval Department composition G, has, at its best, many valuable properties. However, its physical properties are known to vary widely with slight changes in method of manufacture of the castings, such as slight variations in composition, variation in pouring temperature, kind of mold used, method of pouring and gating of molds, size and shape of castings, amount and kind of heat treatment, and so forth.[1] The microstructure of castings made from this alloy is influenced by slight variations of composition, rate of cooling, and kind and length of heat treatment. This is best understood by reference to the equilibrium diagram. The part of the diagram in which we are interested and the effect of the thermal equilibrium relations on the physical properties of the alloy 88 copper, 10 tin, 2 zinc, have been discussed by Hoyt, Campbell, Primrose, and Rawdon.[2]

In Fig. 1 is given the equilibrium diagram of the copper-tin alloys. Briefly stated, the relations of composition and temperature changes are as follows. Compositions between A and a consist of but one constituent—the α bronze, which is a solid solution of copper and tin, rich in copper. On cooling from the molten state these compositions gradually crystallize, at temperatures above 790°, into a mass of interwoven tree-like crystals or dendrites. The cores of the dendrites are rich in copper and the percentage of tin gradually increases as the surfaces are approached. As cooling progresses, after all the metal has crystallized, no further changes occur in the crystals other than diffusion within the crystals, which tends to erase the dendritic pattern and to render the structure more homogeneous.

* Metallurgical Ceramist, U. S. Bureau of Standards.
† Associate Physicist, U. S. Bureau of Standards.

[1] A. D. Flinn: *Iron Age* (1915) **96**, 1292–3.
C. P. Karr: U. S. Bureau of Standards *Tech. Paper* 59, Pt. 1.

[2] S. L. Hoyt: *Engng.* (1913) **96**, 667–7, 704–5.
William Campbell: *Trans.* Am. Inst. Met. (1912) **6**, 158–172.
H. S. Primrose: *Metal Ind.* (1916) **14**, 202–4.
H. S. Rawdon: U. S. Bureau of Standards *Tech. Paper* 59, Pt. II.

In compositions to the right of α, the first part of the process of crystallization is similar to that just described. At 790° C., the alloy is nearly solid and consists of dendrites of varying composition and a liquid con-

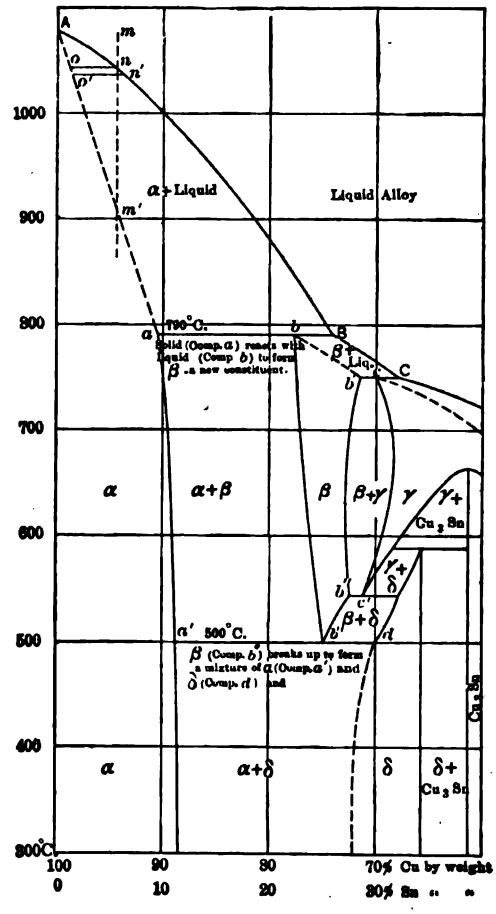


FIG. 1.—STRUCTURAL EQUILIBRIUM DIAGRAM OF COPPER AND TIN.

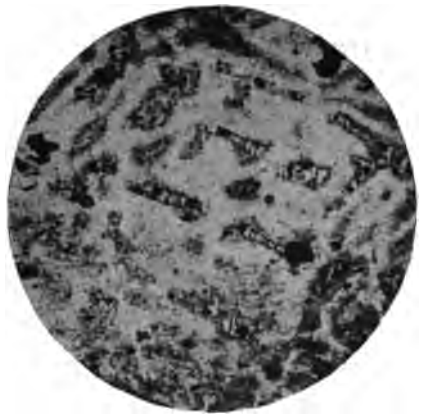
taining 74.5 per cent. copper. At this temperature a reaction occurs between this liquid and some of the already solidified portion to form a solid known as the β solid solution. This β constituent lies in the angles between the interlocking fingers of the dendrites. When the cooling progresses to 500° the β solid solution breaks up into an intimate mixture of α and δ solid solutions. This intimate mixture or eutectoid is known as "bronzite." It is very hard and brittle and therefore has an unfavorable effect on the physical properties of the cast alloy. This type of structure is illustrated in Fig. 2.[3]

[3] H. S. Rawdon: *Loc. cit.*

According to the diagram, compositions between α (approximately 9.5 per cent. tin) and α' (approximately 13 per cent. tin) should be sub-

A. Specimen 19. Remelted and allowed to cool in furnace. Difference in orientation of dendritic structure marks out the various crystals. × 4.

B. Specimen 19. Dark portions are cores rich in copper; light angular spots are hard brittle eutectoid inclusions. × 85.



C. Specimen 568. Shattering of eutectoid under strain is illustrated. × 85.

D. Specimen 568. Cracks (black) in eutectoid (white) are at right angles to direction of strain. × 212.

FIG. 2.—TYPICAL MICROSTRUCTURE OF CAST ZINC-BRONZE (88–10–2). *A* AND *B* WERE ETCHED WITH AMMONIUM HYDROXIDE CONTAINING HYDROGEN PEROXIDE; *C* AND *D* WITH AMMONIACAL COPPER-AMMONIUM CHLORIDE.

ject to the reaction mentioned as taking place at 790° with formation of some β solid solution and on further cooling should gradually change com-

pletely to the α solid solution without the formation of any eutectoid at 500° C. Actually these compositions may do this or they may crystallize in the manner described for either of the two other classes of compositions.

In spite of the great amount of study the alloys of copper and tin have received, there is no well-defined agreement in regard to the limit of the α solution. It varies from 5 per cent. tin in Giolitti's[4] diagram to 13 per cent. in Shepherd's.[5] The percentages shown are by Gulliver[6] and represent condition of equilibrium obtained either by excessively slow cooling of the molten alloy or by reheating an alloy which solidified by cooling at an ordinary rate.

As emphasized by Hoyt,[7] the addition of small quantities of zinc do not materially alter the structure of the copper-tin alloys rich in copper. Guillet[8] has determined experimentally that as far as structure is concerned one part of zinc is equal to one-half part of tin. If we adopt Guillet's suggestion we may consider that the 88–10–2 alloy is equivalent in structure to a copper-tin alloy containing 11.1 per cent. of tin. This places the alloy in that part of the diagram lying between the points α and α', the location of which are debatable and which limit a field of compositions that are apt to crystallize in a very erratic way, depending on conditions. This conclusion is borne out by microscopic examination of castings of the 88–10–2 alloy. In the case of forty-five specimens, selected at random from over a thousand, Rawdon[9] found no eutectoid in a few cases, small to moderate amounts in others, and a great abundance in still others. While according to Rawdon the presence of oxide films in the castings was the predominating factor in producing castings with poor physical properties, variations in the amount of eutectoid present and in the general type of crystalline structure were accompanied by marked variation in the physical properties of the alloy.

As a means of conserving tin during the war, the Sub-committee on Bearing Metals of the American Institute of Mechanical Engineers suggested the use of 90 copper, 6.5 tin, 1.5 lead, 2 zinc, in place of the 88–10–2 alloy commonly used. The committee stated[10] that the proposed alloy "is stronger and more reliable; is more economical in foundry production; is easier and more satisfactorily machined; for hydraulic work is less liable to leaks; in steam service it is from 5 to 40 per cent. stronger than the old composition; while at the same time this substitute formula offers a saving of 3½ per cent. of tin, which is always wasted in the old

[4] Giolitti and Tavanti: *Gaz. Chim.* (1908) **38**, 209.
[5] Shepherd and Blough: *Jnl. Physik. Chem.* (1906) **10**, 515.
[6] Gulliver: "Metallic Alloys," 249. Lippincott, 1908.
[7] *Jnl.* Inst. Metals (1913) **10**, 235.
[8] *Rev. de. Met., Mem.* (1906) **3**, 243.
[9] *Loc. cit.*, 56–60.
[10] *Jnl.* Am. Soc. Mech. Eng. (1918) **40**, 854.

formula incident to the production of an inferior alloy." On Dec. 14, 1918, Admiral D. W. Taylor asked the Bureau of Standards to investigate this composition to determine its fitness as a substitute for 88–10–2 alloy. The investigation of the alloy seemed to offer promising possibilities. It has been known since the dawn of the art of metallurgy that small amounts of lead improved the ductility and working properties of bronzes, its use being known to the ancient Assyrians.[11] The advantages of its employment have been noted by many modern writers.[12]

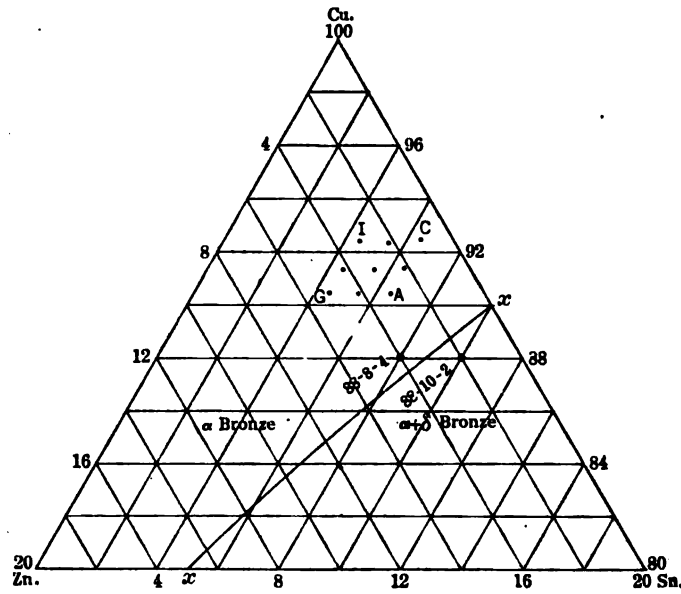


FIG. 3.—COMPOSITION DIAGRAM.

Following the method of Guillet[13] we may consider the copper-tin-zinc content of this alloy as equivalent, as far as production of structure is concerned, to a copper-tin-alloy containing 7.7 per cent. of tin. Since lead is known to be non-soluble in solid solutions of copper and tin and of copper and zinc, it must be considered simply as a mechanical addition. We may thus locate the alloy on the copper-tin equilibrium diagram (Fig. 1) and on doing so we find it falls well within the area of α bronzes that crystallize in comparatively constant and simple manner at high temperatures and undergo no marked transformations during further

[11] Z. Agnew: *Chem.* (1914) **27**, I, 512.

[12] Hanns v. Miller: *Metallurgie* (1912) **9**, 70.
H. S. Primrose: *Jnl.* Inst. Met. (1914) **12**, 254.
Oregowsky and Spring: *Proc.* Int. Cong. for Testing Materials, 6th Congress, N. Y. Sec. VII.

[13] L. Guillet: *Loc. cit.*

cooling. Alloys crystallizing in this manner are much more apt to give castings with uniform physical properties in foundry practice than an alloy with the erratic crystallization behavior of the 88–10–2 alloy.

In order to cover the field of probably useful alloys of this type, it was decided to investigate nine compositions. These in percentages as

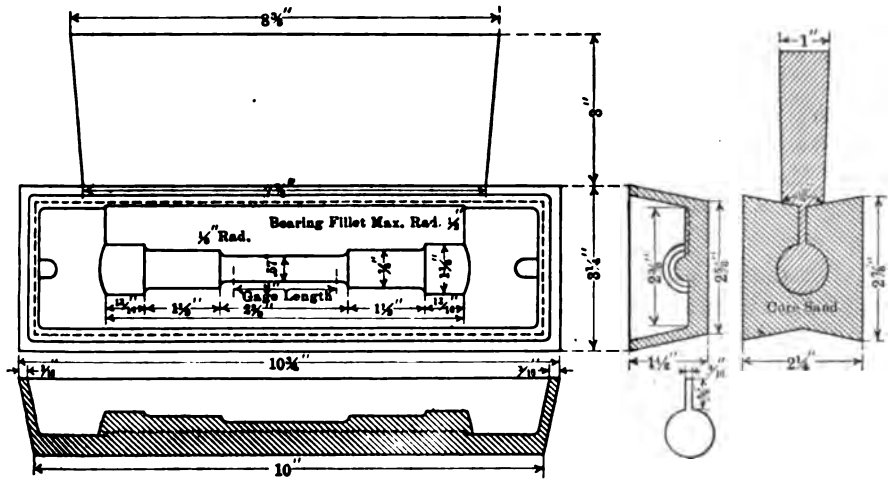


FIG. 4.—CORE BOX USED IN MAKING SHOULDERED TEST BARS.

charged and calculated on the basis of Cu + Sn + Zn = 100, together with their equivalent compositions according to Guillet are given in Table 1. It will be seen that the series of compositions can be divided into three groups, according to tin content, and each group contains three members, characterized by a certain lead content. The locations

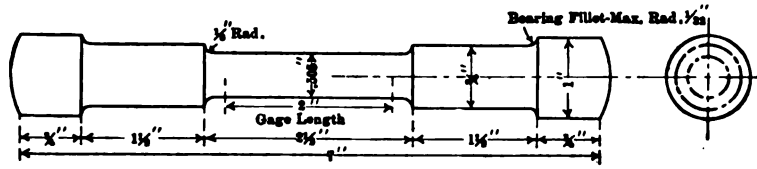


FIG. 5.—SHOULDERED TEST BAR AFTER MACHINING.

of the various compositions, on the basis of Cu + Sn + Zn = 100, and also of the 88–10–2 and 88–8–4 alloys are shown on a triaxial composition diagram in Fig. 3. This method of presentation is more satisfactory than the use of the copper-tin equilibrium diagram and equivalent compositions since it does not involve the use of assumptions. The position of the line x–x is taken from the work of Hoyt.[14] It should be remem-

[14] *Loc. cit.*, 253.

TABLE 1.—*Composition of Alloys Studied*

Alloy	Compositions Charged				Equivalent Compositions			Compositions on Basis of Cu + Sn + Zn = 100			
	Cu	Sn	Zn	Pb	Cu	Sn	Pb	Cu	Sn	Zn	Pb
88–10–2	88	10.0	2	...	88.9	11.1	....	88.0	10.0	2.0	
88– 8–4	88	8.0	4	...	89.8	10.2	....	88.0	8.0	4.0	
A	90	6.5	3	0.5	91.8	8.2	0.51	90.45	6.50	3.05	0.50
B	90	6.5	2	1.5	92.3	7.7	1.54	91.37	6.60	2.03	1.52
C	90	6.5	1	2.5	92.8	7.2	2.58	92.30	6.66	1.04	2.56
D	90	5.5	4	0.5	92.3	7.7	0.51	90.45	5.53	4.02	0.50
E	90	5.5	3	1.5	92.8	7.2	1.55	91.37	5.58	3.05	1.52
F	90	5.5	2	2.5	93.3	6.7	2.59	92.30	5.64	2.06	2.56
G	90	4.5	5	0.5	92.8	7.2	0.52	90.45	4.52	5.03	0.50
H	90	4.5	4	1.5	93.3	6.7	1.55	91.37	4.56	4.07	1.52
I	90	4.5	3	2.5	93.75	6.25	2.60	92.30	4.62	3.08	2.56

bered that the line of compositions *I–C* carry an addition of 2.56 parts of lead, the next line 1.52 parts, and the line *G–A* 0.50 parts.

Eight heats of each of the four test specimens were made of each composition. The method of making and pouring the molds was the one that had been found satisfactory for the 88–10–2 alloy.[15] The making of the core sand molds was greatly facilitated by the use of core boxes with considerable draft instead of boxes with perpendicular sides, as described in the article referred to. The expense of preparing the specimens for testing was materially reduced, without affecting the accuracy of the tests, by casting the specimens with shoulders and using split rings for holding them in the testing machine. This obviated the necessity for cutting threads on the ends of each specimen. The type of test bar and core sand mold used are shown in Figs. 4 and 5.

A summary of the determinations of the physical properties of the specimens thus far tested is given in Table 2. For the sake of comparison, results obtained with the alloys 88 copper, 10 tin, 2 zinc, and 88 copper, 8 tin, 4 zinc, are given also. Attention is called to the following points shown by the data in this table.

Effect of Pouring Temperature.—Higher values were obtained with metal poured below 1150° C. than with metal poured above that temperature. Composition *D* is an exception in that the values were about the same. A satisfactory pouring temperature for test bars made in the manner here described of the compositions employed is 1100° C. (approximately 2000° F.).

Effect of Heat Treatment.—The heat treatment employed raised the proportional limit of all compositions slightly. In respect to other physical properties the effect of heat treatment was slight or detrimental. Since all the compositions used fall in the field of α bronze on the equilib-

[15] C. P. Karr: Five Foundry Tests of Zinc Bronzes, this volume.

TABLE 2.—*Averaged Results of Physical Tests with Mean Deviations*
(All specimens were cast approximately to size, horizontal, in baked core-sand molds with reservoir gates)

Composition	Number of Specimens	Pouring Temperature Range, Degrees C.	Proportional Limit, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Number of Bad Breaks Due to Segregation
88-10-2	6	1,100 to 1,140	13,100 ±1,050	43,100 ±3,350	29.7 ±4.5	24.3 ±2.2	
88- 8-4	6	1,100 to 1,140	11,900 ± 900	43,300 ±1,850.	36.0 ±4.5	28.0 ±4.5	
A	12	1,090 to 1,125	12,200 ± 650	40,700 ±1,500	37.6 ±6.4	34.1 ±4.5	
	12	1,170 to 1,200	12,900 ± 900	37,600 ±2,200	28.1 ±4.4	29.7 ±3.7	
	8[a]	1,090 to 1,200	13,300 ±1,200	35,700 ±3,200	24.9 ±4.8	23.2 ±5.9	1
B	20	1,030 to 1,136	12,300 ±1,400	40,700 ±2,200	35.3 ±8.7	31.8 ±6.0	
	3	1,170	10,400 ±1,050	35,900 ±4,800	25.5 ±8.0	32.5 ±6.0	1
	8[a]	1,080 to 1,170	13,700 ± 800	41,300 ±1,500	37.2 ±6.1	33.6 ±3.7	
C	12	1,100 to 1,140	13,200 ±1,100	39,600 ±3,200	27.2 ±6.5	27.7 ±5.7	
	12	1,150 to 1,200	12,400 ± 950	33,600 ±3,850	18.6 ±9.5	19.7 ±9.8	3
	8[a]	1,100 to 1,200	14,000 ±1,030	34,700 ±4,050	20.1 ±7.9	23.5 ±7.2	2
D	14	1,060 to 1,120	12,400 ±1,100	37,900 ±2,600	29.3 ±5.6	30.4 ±5.5	
	9	1,160 to 1,180	11,500 ± 650	37,700 ±3,400	31.6 ±6.3	32.4 ±5.2	
	8[a]	1,060 to 1,180	13,250 ± 960	37,100 ±1,300	24.2 ±4.9	27.3 ±4.3	
E	18	1,060 to 1,140	10,650 ± 900	36,200 ±3,850	31.4 ±8.3	28.4 ±10.8	1
	6	1,160 to 1,180	9,700 ± 400	30,900 ±2,300	22.8 ±6.5	18.6 ±3.3	1
	8[a]	1,060 to 1,180	11,900 ±1,250	36,000 ±3,300	28.5 ±4.9	26.7 ±6.1	
F	6	1,100 to 1,120	10,850 ± 750	35,900 ±5,300	23.9 ±3.1	22.6 ±3.4	1
	12	1,160 to 1,180	9,900 ± 600	33,700 ±3,100	23.3 ±4.7	23.4 ±6.1	
	5	1,240 to 1,260	9,550 ±1,150	29,700 ±2,900	15.5 ±3.5	16.6 ±4.1	
	6[a]	1,100 to 1,260	10,450 ± 700	33,500 ±3,600	22.2 ±3.4	22.8 ±6.2	2
G	14	1,100 to 1,140	9,100 ± 800	34,700 ±2,300	29.4 ±5.7	25.3 ±5.9	2
	8	1,150 to 1,180	9,200 ± 550	32,800 ±3,700	27.4 ±7.2	24.4 ±7.7	3
	8[a]	1,100 to 1,180	9,550 ±1,050	32,100 ±3,800	28.8 ±4.3	21.9 ±4.3	4
H	21	1,100 to 1,140	8,900 ± 550	33,600 ±2,400	26.5 ±4.5	22.9 ±4.3	3
	3	1,180	8,200 ± 950	28,700 ±1,300	18.3 ±3.6	18.8 ±1.2	3
	8[a]	1,100 to 1,180	10,200 ± 750	31,700 ±2,600	24.2 ±2.7	20.6 ±3.6	1
I	Tests not complete at date of writing						

[a] Heat treated. Specimens were raised to 600° C. in 50 min., maintained at that temperature for 30 min., and then allowed to cool in furnace, in 12 hr., to room temperature.

rium diagram, we cannot expect heat treatment to have any marked effect unless the temperature is raised to the point where the lead, which is held in mechanical suspension, flows in the pores of the copper-zinc-tin alloy.

Effect of Substitution of Zinc for Tin.—Comparing the corresponding numbers of the groups *ABC*, *DEF*, and *GHI* poured at the same temperature shows that, in general, this substitution produced lower values in physical tests. This is not in accord with the data shown for the alloys 88–10–2 and 88–8–4.[16] It should be remembered that in the latter case substitution of zinc for tin moved the composition over the line separating the field of α bronze from that of α and δ bronzes.

Effect of Substitution of Lead for Zinc.—A comparison of the three members of each group shows that this substitution resulted in lower values.

Effect of Substitution of Lead for Tin.—A comparison of composition *A* with *E*, *B* with *F*, and *D* with *H* shows that substitution gave markedly lower values.

Segregation.—The number of bars showing segregation increased from group to group as the groups became richer in zinc and poorer in tin. Within the groups segregation increased with increase of lead and decrease of zinc.

Place of Lead-zinc Bronze B in the Series.—This is the composition recommended by the Committee of the American Society of Mechanical Engineers; it is surpassed by lead-zinc bronze *A* only.

Equivalent Compositions.—In order to avoid any misconception in regard to the term equivalent compositions it should be called to mind that Guillet applied this term to signify structural equivalence only. The compositions are not equivalent as far as physical properties are concerned. For instance, lead-zinc bronzes *B* and *D* have the same equivalent compositions except that *B* contains more lead than *D*. If the compositions were truly equivalent otherwise, this variation should make *B* the weaker metal, but the reverse is actually the case according to the physical tests. A similar example is found in the case of lead-zinc bronzes *C*, *E*, and *G*.

The data for six test specimens of the 88–10–2 alloy given in the table do not furnish sufficient basis for comparison of the lead-zinc bronzes described with that alloy. A lot of thirty-two test specimens of the 88–10–2 alloy has been prepared in the Bureau of Standards' foundry in the manner employed in preparing the lead-zinc bronzes. When these are tested, a comparison can be made. From the data available[16] it is possible to predict that the best of the lead-zinc bronzes, compositions *A*, *B*, and possibly *D*, will probably be found superior to the 88–10–2 alloy in ductility and about equal to it in other respects.

[16] See also C. P. Karr, this volume.

Qualitative tests of the machining properties of these metals were made in the Bureau of Standards machine shop. It was found that all the lead-zinc bronzes had good machining qualities being free cutting and giving short thick chips of metal with cutting tools. The ease of machining increased from group to group as tin decreased and zinc increased. Within the groups the thickness of the chips increased with increase of lead. While lead-zinc bronze *A* gave the thinnest chips of the lead-zinc bronzes, still it was a much more free-cutting material than the alloy 88 Cu, 8 Sn, 4 Zn, which in the same tests gave shavings about 1 in. long. The latter, in turn, was superior to the 88–10–2 alloy, which gave thin shavings up to 8 in. in length.

In this investigation it has been shown rather conclusively that, with this copper content, increase of either lead or zinc has unfavorable effects on the physical properties of the alloys. Moreover the most satisfactory composition *A* tested is at one corner of the series. It is desirable therefore to investigate a new series of compositions containing less lead and zinc than lead-zinc bronze *A*. Such an investigation is being planned by the Bureau.

Summary

The salient points of this investigation may be summarized as follows:

Of nine variations in composition of lead-zinc casting bronzes containing 90 per cent. copper studied, the most satisfactory was lead-zinc bronze *A* containing 90 copper, 6.5 tin, 0.5 lead, 3 zinc. This composition showed a proportional limit of 12,200 ± 650 lb. per sq. in., tensile strength 40,700 ± 1500 lb. per sq. in., elongation in 2 in. of 37.6 ± 6.4 per cent., and reduction in area of 34.1 ± 4.5 per cent.

Substitution of lead, above ½ per cent., for zinc or tin and of zinc, above 2 per cent., for tin was found to have detrimental effects on the physical properties of the castings.

A pouring temperature of 1100° C. (approximately 2000° F.) was ound satisfactory for these lead-zinc bronzes.

Heat treatment had but slight or detrimental effect on these bronzes.

The results obtained have justified the prediction of the qualities of the alloys by *a priori* reasoning based on the copper-tin equilibrium diagram.

The writers wish to acknowledge their indebtedness to Mr. R. S. Johnston and Miss H. C. Baker, of the Engineering Materials Testing Laboratory of the Bureau of Standards, for suggestions in regard to the shoulder type of test bar and for the painstaking care used in testing the specimens.

DISCUSSION

W. M. CORSE, Mansfield, Ohio.—Outside of the commercial valuation of the material, for what purpose does this alloy—90 per cent. of copper, 6½ per cent. tin, 2 per cent. zinc, and 1½ per cent. lead—seem to be eminently fitted?

C. P. KARR.—So far as our tests go, it would be eminently fitted for steam valves and pistons, and for the work for which 88–10–2 bronze is generally used, although for very large castings it would not be superior to 88–8–4 bronze.

P. E. MCKINNEY,* Washington, D. C.—Some time back, due to a desire to avoid some of the objectionable features of 88–10–2 bronze, particularly on heavy castings, also to save tin where possible, we took up the question of a substitute for 88–10–2 bronze, where red bronze was ordinarily specified. After trying most of the mixtures, we found that when using as low a tin content as is given in this proposed composition, one very valuable property of general red-bronze casting construction is sacrificed; namely, its excellent bearing properties and rigidity. In other words, the material has a lower Brinell hardness than either the 88–10–2 or the 88–8–4 bronze, and when used as a bearing (of course, we are not speaking of even 88–10–2 as a bearing metal for extreme service) there is a tendency on the part of the softer alloys to pick up. On the other hand, the 88–8–4 bronze gives practically the same Brinell hardness as the 88–10–2 and has sufficient bearing properties and superior water-tight properties in castings of anything but very thin cross-section; that is, a heavy casting of any kind, when made from a carefully prepared alloy of 88–8–4 is probably an ideal water-tight casting, particularly if a little lead is introduced to close the grain. The effort to reduce the tin content in the casting is very necessary. Even this 6 per cent. of tin would be far superior, because there is no excess of tin to form a beta constituent.

It would be a good proposition if everybody interested in the use of red bronzes would conduct experiments, from time to time, with the introduction of nickel. Nickel seems to have some excellent properties. With a reduction of the tin and letting the zinc remain low, nickel seems to toughen the bronze; in addition to tin, it gives a very desirable combination of toughness and hardness. At this time there is a very good commercial reason for considering the use of nickel in the red alloys. As a result of the war, there is a lot of material that would be perfectly good casting copper if it were not contaminated with nickel, due to the manufacture of rotating bands for shells of various calibers.

* Chemist and Metallurgist, U. S. Naval Gun Factory.

The utilization of these cupro-nickel alloys, that is, alloys containing from 1 to 3 per cent. of nickel, would offer a very economical method of introducing copper into these alloys.

I feel that this question should be taken up by foundries producing heavy castings, because while results obtained from test bars are extremely valuable and show what can be obtained under standard conditions, you cannot get the same results in a heavy casting that you can in the small casting made in a miniature cross-section.

R. F. Wood,* Sandusky, Ohio.—Mr. Karr's alloy B is very similar to an alloy that I have used for the past couple of years with 1 per cent. nickel substituted for 1 per cent. of the copper, and in making castings of about 3000 lb. weight it has given very good results in producing water-tight castings.

C. P. Karr.—Have you made any test bars of the metal in question, and if so, will you give us the results?

R. F. Wood.—I have a much less complete set of results than I wish I had, but in regard to its water-tightness I can say that it worked very nicely. The following shows some typical results.

Weight of Casting	Ultimate Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Copper, Per Cent.	Tin, Per Cent.	Lead, Per Cent.	Zinc and Nickel, Per Cent. by Difference
1000	44,600	17,400	28.0	89.30	6.59	1.72	2.39
	32,100	25,000	5.0				
4020	41,100	24,900	21.0	87.41	7.10	1.55	3.94
	42,500	25,000	25.0				

The second tensile test broke outside the gage marks.

C. P. Karr.—What hydraulic pressure was used?

R. F. Wood.—These castings were ½ in. thick, were tested to 150 lb. without backing, and carried about 2000 or 3000 lb. pressure, backed.

* Metallurgist, Sandusky Foundry & Machine Co.

Relationship of Physical and Chemical Properties of Copper

By Frank L. Antisell,* Perth Amboy, N. J.

(New York Meeting, February, 1920)

Certain physical and chemical properties of copper are so intimately related that a change in variation of the physical properties indicates a certain chemical change. The standard specifications of copper of the American Society for Testing Materials are based upon physical characteristics with one exception, namely, the copper contents. The physical standard includes electrical properties, defects in the "set or casting," variation in dimensions, weight, etc. Paragraph 4 of the specifications states, "Wire bars, cakes, slabs and billets shall be substantially free from shrink holes, cold sets, pits, sloppy edges, concave tops, and similar defects in set or casting." Shrink holes and concave tops indicate both physical and metallurgical defects; cold sets, sloppy edges, etc., indicate physical defects only; small pit holes may be indicative of either or both physical and metallurgical defects, depending on conditions under which they originated.

To the refiner, a copper casting, no matter how made, is known as a "shape," irrespective of whether it is wire bar, ingot, cake, slab, billet, etc. As practically all shapes are cast in an open mold, that is a mold without cope, the surface of the shape cools in contact with the atmosphere and has a coating of oxide. Certain phenomena of the surface indicate the adaptability of the metal for forging or rolling. The writer believes that it is much simpler to produce shapes that are metallurgically correct than those that are mechanically satisfactory. When copper is to be rolled into thin sheets or drawn into very fine wire, the slightest physical defect becomes evident. It is, therefore, of the utmost importance to consider every characteristic of the shape and ascertain the physical and chemical relationship.

Pitch and Set.—The appearance of the surface of the copper when cooled is considered as to its "pitch," or the general contour of the surface of the shape (which may vary from a concave to a convex); and the "set," or the detail appearance of the surface of the shape (the wave-like structure). When the shape presents a concave surface, it is known as "low pitch;" a convex surface is known as "high pitch" or "tough pitch;" and a level surface is called "flat pitch." The set of the copper is, in a very large measure, directly related to the pitch; and so intimately are

* Superintendent Raritan Copper Works.

these characteristics connected that they are often used as synonymous terms by the refiner when he is speaking of well-refined copper. If, however, he is speaking of unhealthy or improperly refined copper, he will define both the pitch and the set. The character of the set will show whether the copper is low pitch but healthy, or low pitch but unhealthy and must be refined again. High-pitch copper is usually described in terms of the set. If the set is very close and even, the copper contents are about 99.95 per cent.; this close set cannot be produced on a shape with a low pitch.

As the shape cools, there is a constant contraction with some degassing of the metal. As the top surface of the shape freezes, there is a tendency for the thin layer of copper to assume a finely corrugated surface at right angles to the longitudinal axis of the shapes; while the gassing of the metal tends toward the formation of a coarse wave-like structure. This structure varies, with the metallurgical properties of metal, between the extremes of a finely corrugated irregular surface, set or close grain, to a comparatively smooth surface in which the ridges are a considerable distance apart and the grain is coarse.

Influence of Oxygen on Copper.—Metallurgically, the copper presents the best general characteristics when shapes of a certain size present a slightly convex contour, high pitch, with a good set and close grain. While a shape of a certain weight presents a satisfactory appearance, it does not follow that larger or smaller shapes will be the same. As a general rule, the thicker the shape, the less oxygen is permissible in it; the thinner the shape the more oxygen may be present. Oxygen is, therefore, often spoken of as a medicine for copper, it being used to regulate the pitch. While the pitch may be flat or slightly convex, it may be decidedly inferior if it presents a coarse grain.

Copper containing an excessive amount of oxygen that is introduced during the refining period is known as "set" or "dry copper." As the amount of oxygen decreases and approaches the analysis of satisfactory metal, it is known as underpoled; and when it is thoroughly refined, it is known as tough pitch. The fracture of tough copper must exhibit a decided metallic luster; a brick-red shade is indicative of undesirable oxygen contents.

With low oxygen contents, copper may be heated over a long period with the formation of a very slight coating of oxide, while with higher oxygen contents, the copper oxidizes quickly.

Influence of Sulfur on Physical Properties.—The general physical properties of copper change in a marked manner with the increase of sulfur. An increase in the sulfur contents affects the number of bends in a very much greater ratio than does oxygen.

Unhealthy Copper.—Unhealthy copper contains slight quantities of gases, such as hydrogen, carbon monoxide, sulfur dioxide, and carbon diox-

ide. If an attempt is made to remove the excessive oxygen, the copper will spew; that is, a miniature volcanic action will occur in the shape and the copper will be known as overpoled. Copper in this state will be low in electrical conductivity and have a small reduction in area, due to several reasons, particularly the excess of oxygen. These properties can be improved only by subjecting the entire charge to a refining process, which consists of oxidizing the copper, thus removing the reducing gases, and then poling the copper up to a tough pitch. Unhealthy copper may present either a high or a low pitch, but if an attempt is made to raise the low pitch, the copper will spew.

Reasons for Rejecting Copper.—Reasons for rejecting refined copper on physical examination are: Low pitch; overpoling; cold sets; spewing; shot; fish (slivers of foreign copper, as the fins from the pouring ladle, etc.); holes of several characters, as water holes, shake holes, shrink holes, gas holes, spew holes, general porosity; foreign substances, such as charcoal, bone ash, dirt, etc.; splashes; fins; cracks; large set marks; water bursts; ridges on surface; shapes cast in rough molds; wrong dimensions; and collective defects. By the last term are meant two or more slightly developed defects, one of which would not be a sufficient cause for the rejection of the shape.

A definite individual hole in the set, or a "spot" as it is termed, is indicative of excess of oxygen; while the series of small pit-like holes along the center of the shape is an indication of overpoled copper.

If the chemical analysis is standard and the pitch and set are good, there should be an examination for porosity, which is discovered just under the skin of the shape by cutting with a sharp chisel—the metal should show a dense surface and substantially be free from porosity—and the character and reason for the holes in the shape. If the holes were shaken in, the shape will not be satisfactory for drawing into fine wire or for rolling into very thin sheets. This defect is caused by the vibration of the mold allowing liquid copper to surge back and forth when it is cooling, resulting in slip bands when the shape contracts in cooling. This internal fracture between the grains of copper may be present even though there may not be any outward indications.

Copper, generally, is cast in molds that are carried by a machine under a ladle and it was deemed impossible at one time to move a mold of molten copper with sufficient smoothness to eliminate this washing of the metal in the mold and produce a perfectly sound casting. Prof. A. L. Walker has invented an apparatus with which shapes can be successfully poured. So important is this question of moving the molds of molten metal that casting machines have been introduced in the refineries that weigh as much as 300,000 lb. (Clark machine) in which the vibration is reduced to a minimum by a highly organized mechanical design.

Analysis of Electrolytic Copper.—Good electrolytic copper should analyze approximately as follows: copper, 99.950 per cent.; silver, 0.0010 per cent.; oxygen, 0.0390 per cent.; sulfur, 0.0030 per cent.; arsenic, 0.0015 per cent.; antimony, 0.0020 per cent.; nickel, 0.0015 per cent.; iron, 0.0025 per cent.; lead, nil; bismuth, nil; selenium, trace; tellurium, trace. The specifications of the American Society for Testing Materials permit a metallic contents of copper plus silver of 99.88 per cent. In every refinery, no matter how carefully conducted, an occasional furnace charge will not do better than to meet this analysis, the decrease being due generally to the combination of sulfur, oxygen, and iron.

Electrical Conductivity.—The electrical conductivity of copper is considered the most convenient method of determining its general properties. The conductivity varies in inverse ratio to its oxygen contents, and is directly proportional to the number of bends, a function of its reduction in area. The bends are determined on 12-gage wire by the Capp machine, a simple device that bends a wire at an angle of 90° until it is broken. The general relationship of various physical properties of the oxygen contents are shown in Table 1. This table is based upon a series of tests in which the sulfur contents is about 0.002 per cent. The copper in the series *J* analyzes 99.97 per cent.

TABLE 1.—*General Law Relating to the Influence of Oxygen on Properties of Annealed Copper. Determined on No. 12 Soft Wire*

	Oxygen Contents, Per Cent.	Tensile Strength, Pounds per Square Inch	Elongation, Per Cent.	Conductivity, Per Cent.	Number of Bends
A	0.200	37,340	28	98.25	21
B	0.175	37,300	29	98.60	22
C	0.150	37,050	30	98.83	23
D	0.125	36,850	31	99.20	24
E	0.100	36,600	32	99.55	25
F	0.075	36,300	34	99.80	27
G	0.050	36,000	35	100.30	30
H	0.025	35,200	36	100.60	33
J	0.015	34,000	37	100.80	35

Laws Governing Tough-pitch Period.—A few general laws may be stated for the tough-pitch period, with reference to the relative properties of copper, which are applicable over a short range only.

1. As the tensile strength increases, the conductivity decreases.
2. As the oxygen contents increases, the tensile strength increases
3. As the tensile strength increases the elongation decreases.
4. As the oxygen contents increase, the resistance of bending decreases.

Annealing Copper.—Proper care in the annealing of copper is often neglected, and it is seldom that the maximum elongation is realized, which is very necessary where the metal must stand a large amount of work in being fabricated. Extremely tough-pitch copper exhibits great ductility, and if it is given improper treatment in the mill it may tend to shred or tear the surface of the copper. These metallic shreds or slivers will not be entirely torn from the main body, but will adhere to it at one end.

When such a piece of copper is pickled, the shreds, not being oxide, do not dissolve in the solution, thus resulting in an imperfect surface. If the copper is not so tough, these slivers may be entirely detached or will not be formed at all, due to the thick veneer of scale. While copper may occasionally be preferred with such properties, it is at the expense of the physical characteristics of copper.

DISCUSSION

THE CHAIRMAN (W. H. BASSETT,* Waterbury, Conn.).—Copper is one of the most important, perhaps the most important, metal that the non-ferrous metallurgist has to consider, particularly if we think of the volumes of materials used in the arts. The refining of copper for a long time was in the hands of the Welshmen and Cornishmen, who started the industry in this country, and matters of pitch and set were secrets. The refiner's buttons were carefully kept from the observation of every one and thrown back into the furnace as soon as the refiner had seen the break. In recent years, we have had various papers explaining these matters and now metallurgists know what constitutes good copper; but, unfortunately, this knowledge is not always taken advantage of and too much copper is made with high oxygen, or which the refiner has attempted to get by in the "unhealthy" state, or which has not been cast as it should have been. All of the defects that Mr. Antisell has pointed out are apparent to those who have to roll copper into perfect sheets, or draw copper into wire, particularly fine wire.

Mr. Antisell has touched upon an important point by his statement that "proper care in the annealing of copper is often neglected."

G. V. CAESAR,† Plainfield, N. J.—It is my experience that while the average mill foreman recognizes the necessity for close control of heat when brass shapes are being treated, in the case of copper there is a tendency to use any temperature short of actual melting. It has been shown conclusively that the elongation and reduction of area commence to decline in the neighborhood of 700° C.; this temperature should not be exceeded, if the highest possible degree of ductility is desired. Another

* Technical Superintendent and Metallurgist, American Brass Co.

† Metallurgist, British American Metals Co., Inc.

important consideration is the necessity for maintaining oxidizing conditions in the furnace. A comparison of the physical properties of deoxidized copper and the properties in the table the author has presented would be of great value.

W. R. WEBSTER,* Bridgeport, Conn.—The standards of the copper manufacturers appear to have declined in the last 25 years. I am confident that the copper made by the old Bridgeport Copper Co. 25 years ago averaged materially better than the copper ordinarily obtainable on the market today. The reason I attribute for this situation is the well-known difference between well-done handwork and machine work that is not so well done. In the old Bridgeport copper furnaces, we succeeded in getting up to 40,000 lb. to a charge; when we reached that amount we thought we had done a real day's work. But Mr. Antisell's furnaces are much larger, as are practically all of the furnaces in use today, and it apparently is much more difficult to keep these large furnaces in condition than it was the smaller furnaces used in former days.

ARTHUR L. WALKER,† New York, N. Y.—Mr. Antisell is correct in stating that the metallurgist has much more difficulty in overcoming the physical than the chemical defects in copper. I would like to offer a correction, however, in regard to his statement relative to the bending test. That test can be considered only when supplemented by a conductivity test, for the reason that copper which contains a small percentage of arsenic will satisfactorily pass the bending test, but will not pass the conductivity test.

In one of the copper refineries in the vicinity of New York, trouble occurred due to cracked wire bars, a shipment of which had been condemned. A microscopic examination showed that the cracks, which occurred in the same position in each bar, were between the grains of copper. It was found that the trouble was due to the method of pouring. As the copper was always poured into the mold at the same place, the molds became hotter at this point than anywhere else, so that the wire bar would freeze at this point after the rest of the casting had solidified. Copper contracts considerably on cooling after solidification and the eutectic, cuprous oxide and copper, which freezes about 20° below the freezing point of copper (1084° C.) is very brittle just below the latter temperature. As a result, after both ends of the bars had solidified the strain due to contraction in cooling was so great at the center that the brittle eutectic between the grains was ruptured. After the casting machine was arranged so that the molten copper was poured along the

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* Vice-president, Bridgeport Brass Co.

† Professor of Metallurgy, School of Mines, Columbia University.

entire length of the molds, there was no more trouble due to cracked wire bars.

F. R. PYNE,* Chrome, N. J.—Mr. Webster has said that the copper made 25 to 30 years ago is more suitable to the manufacturer than the copper of today. This is undoubtedly true of certain kinds of copper for certain uses. In those days copper that received mechanical work was largely used for sheets, staybolts, etc.; at the present time, except that used for alloy purposes, copper is used largely for electrical purposes and is electrolytically refined, whereas 25 to 30 years ago it was furnace refined. The result is that manufacturers are now obtaining a metal that is probably too pure for good mechanical work but is excellent for electrical purposes; the old copper, which had silver, oxygen, and arsenic as a result of being furnace refined, is undoubtedly more satisfactory for mechanical work than the modern much purer material.

W. R. WEBSTER.—Probably 90 per cent. of the copper made by the Bridgeport Copper Co. was turned into wire bars. Our conductivity possibly averaged 0.25 per cent. lower than the general run of refining today, but as far as these mechanical defects are concerned, the quality was much better.

ARTHUR L. WALKER.—When the Baltimore Copper Works was shipping large cakes, weighing from two to three tons, to the Russian Government for firebox purposes, some copper was condemned and a concession asked because it was too soft. It would not stand the wear due to attrition of the cinders against the firebox. The metal was too pure, so it was suggested that a small percentage of arsenic be added to increase the hardness.

* Works Superintendent, U. S. Metals Ref. Co.

A Peculiar Type of Intercrystalline Brittleness of Copper

By Henry S. Rawdon,* Washington, D. C., and S C. Langdon,† Chicago, Ill

(New York Meeting, February, 1920)

The following note describing the behavior of copper under rather unusual conditions is offered for its suggestiveness rather than as a complete study of the question. The examinations described were made because of a request for information concerning the embrittlement of copper when heated in a molten salt bath (sodium chloride) for the purpose of cleaning, as well as softening it. It is well known that metals may be rendered very brittle by electrolytic action in aqueous solutions, in all probability by the action of nascent hydrogen, and it was suspected that perhaps the embrittlement of the copper by means of the molten salt was produced in a somewhat similar manner.

It was found that the copper was in contact with iron (or steel) while immersed in the molten salt, through the occasional use of an iron stirring rod, iron forceps for handling the pieces, and an iron pot for containing the fused salt. In the electrochemical potential series iron and copper stand some distance apart, copper being electronegative to the iron. Assuming that the two metals bear a similar relation to each other, when immersed in a bath of molten salt, as they do in an aqueous solution, they would be expected to form a galvanic couple, the copper being the cathode. By this means the copper might be embrittled, as often happens in aqueous solutions, by the action of the liberated hydrogen. In this case, however, the embrittlement must be attributed to some other agent than hydrogen.

To demonstrate how copper may be embrittled under these conditions, two small rods, one of copper and the other of mild steel, approximately $\frac{3}{8}$ in. (9.5 mm.) in diameter, were immersed in a bath of sodium chloride that had been heated somewhat above its fusion point (melting point of sodium chloride is 801° C.) and an electromotive force of approximately 6 volts from a storage battery was impressed upon the system. The copper was made the cathode and the action was continued for several minutes. When removed from the bath, cooled, and tested for brittleness by bending the specimen back and forth, while clamped firmly at one end in a vise, the copper rod was found to be very brittle, as compared with a rod of the same length of the untreated copper tested

* Physicist, Bureau of Standards.

† Professor, School of Chemistry, Northwestern University.

in the same manner. In a similar set-up, the copper was made the anode of the electrolytic cell and tested for brittleness in the same manner.

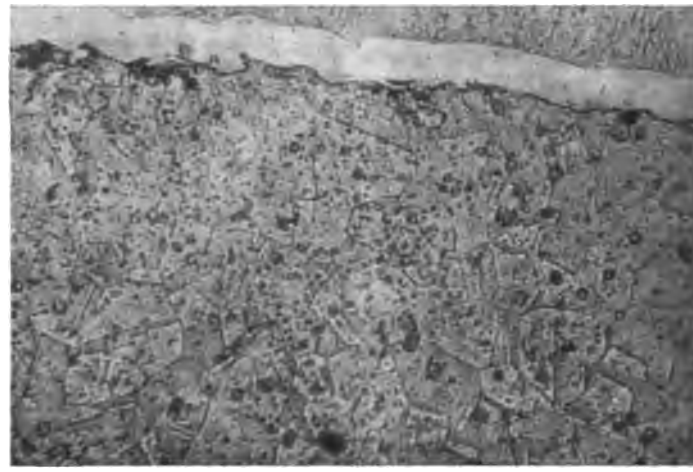


FIG. 1.—INITIAL CONDITION OF COPPER ROD. THE ROD WAS SECTIONED TRANSVERSELY. THE WHITE BAND IS THE LAYER OF NICKEL, WHICH WITH THE ELECTROLYTIC COPPER OUTSIDE IT WAS USED TO PROTECT THE EDGE OF THE SECTION DURING POLISHING. THE DARK SPOTS REPRESENT INCLUSION OF CUPROUS OXIDE. THE ETCHING FLUID WAS CONCENTRATED AMMONIUM HYDROXIDE AND HYDROGEN PEROXIDE. × 500.

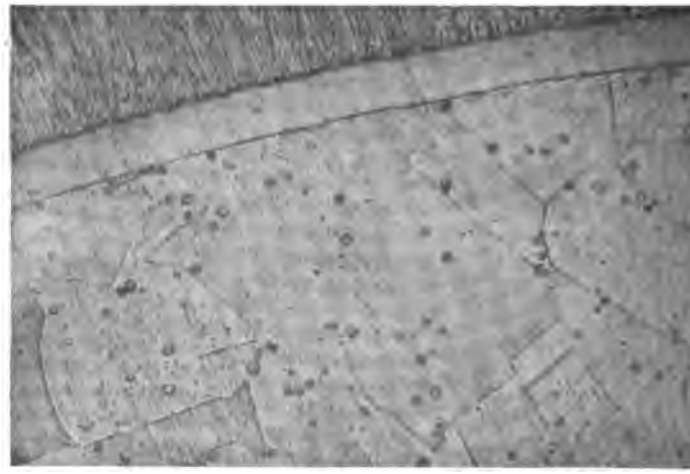
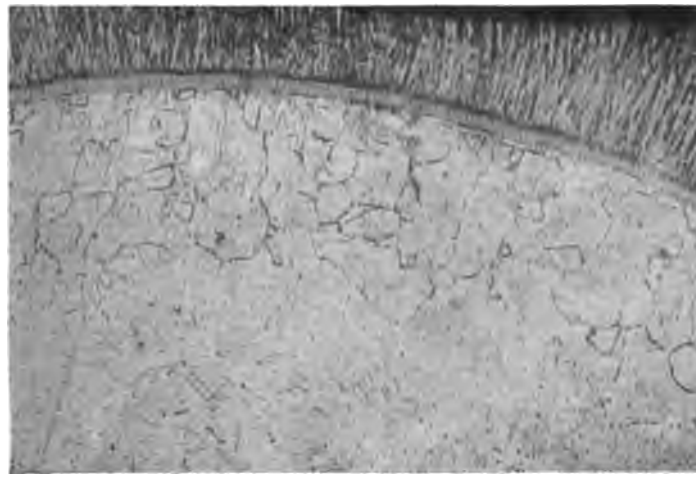


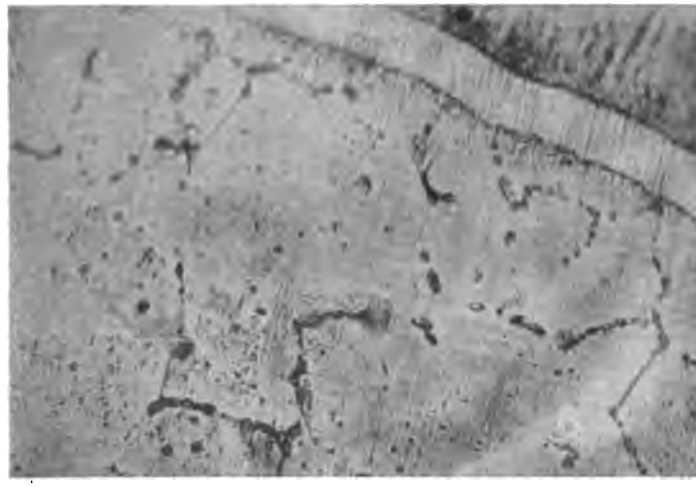
FIG. 2.—COPPER USED AS ANODE IN FUSED-SALT ELECTROLYTIC CELL. THE HIGH TEMPERATURE INCREASED THE GRAIN SIZE CONSIDERABLY. THE EDGE OF THE SECTION OF THE ROD HAS ALSO BEEN SMOOTHED BY THE ETCHING ACTION OF THE FUSED SALT. ETCHING FLUID, CONCENTRATED AMMONIUM HYDROXIDE AND HYDROGEN PEROXIDE. × 500.

In this case the copper proved to be as soft and tough as the original and to require practically the same number of bends to cause it to fracture. It showed no evidence of embrittlement.

Sections of the three rods were examined microscopically in the endeavor to show the cause of the pronounced differences in mechanical properties due to the treatment. The specimens were first plated with



a— × 100



b— × 500

FIG. 3.—COPPER USED AS CATHODE IN FUSED-SALT ELECTROLYTIC CELL. THE SPECIMEN HAS BEEN SLIGHTLY ETCHED WITH THE SAME REAGENT AS IN FIGS. 1 AND 2. A VERY MARKED INTERCRYSTALLINE ATTACK OF THE SURFACE METAL OCCURRED IN THE FUSED SALT BATH, BY WHICH THE GRAIN BOUNDARIES ARE VERY STRONGLY MARKED. THE SURFACE OF THE METAL WAS PROTECTED AS IN FIGS. 1 AND 2.

nickel after which a thick layer of copper was deposited electrolytically. This was done so that when the rods were cut and polished for microscopic examination, the edge would be protected and the structure of the surface metal could be examined readily up to the extreme edge.

The micrographs illustrate the structure of the material in the three conditions. Fig. 1 shows the copper of the rod used. Though not a hard-drawn rod, the final annealing was not sufficient to remove all evidence of distortion of structure due to cold work. The metal pitted rather badly upon etching, due to inclusions of oxide; the surface of the rod appears rather rough at the magnification used (×500) as compared with the same material after treatment in the fused salt.

Fig. 2 shows the copper rod after it was used as the anode in the fused-salt electrolytic cell; the cathode was iron. The surface has been smoothed and cleaned so that the edge of the cross-section is an almost perfect arc of a circle. The structure is that of annealed copper, all evidence of cold-working has been erased. The inclusions of cuprous oxide are still present but are uniformly distributed and the metal shows nothing in its structure suggestive of brittleness.

Fig. 3 shows the copper rod after its use as the cathode. In (*a*) (×100), a well-defined surface layer is to be seen, in which the crystalline boundaries are very strongly defined; they are to be seen even before the metal is etched. In (*b*) is shown the lightly etched specimen at a higher magnification, the intercrystalline or boundary markings are of an appreciable width and are not merely separations between the grains. The cuprous oxide inclusions are also to be seen distributed much the same as in the other specimens. They do not appear as conspicuous in this specimen as in the others, since the metal was etched more lightly.

The probable explanation of embrittlement of the copper when it is made the cathode is that an appreciable amount of metallic sodium is formed by the electrolysis, which immediately alloys with the copper. The most striking feature is the selective attack by which the metal of the grain boundaries is acted upon and the action progresses inwardly between the crystals instead of forming an alloy layer upon the outside of uniform thickness. The behavior of the specimen of Fig. 3, when subjected to the bend test, illustrates the effect of a relatively thin brittle skin upon the properties of a relatively larger piece. The structure of the interior of the specimen shows no evidence of brittleness any more than does that of the rod used as an anode, or the rod in its initial state. It may be assumed, therefore, that only a relatively very thin skin has been rendered brittle by the electrolytic action, the properties of the entire rod have, however, been very profoundly changed.

Discussion of this paper begins on p. 458.

Intercrystalline Brittleness of Lead

By Henry S. Rawdon,* Washington, D. C.

(New York Meeting, February, 1920)

The relation between the course, or path, of the fracture of metals and alloys, produced in service or as a result of certain laboratory tests, and the crystalline units of which such materials are composed is of utmost importance. The fracture of normal material is, in general, intracrystalline, *i.e.*, it consists of a break across the grains rather than of a separation between them. An intercrystalline fracture indicates either that the metal is of very inferior quality or that the break occurred under very unusual conditions, *e.g.*, at a very high temperature. The usual mechanical tests, when applied to metals of the type that breaks with an intercrystalline fracture, merely measure the coherence of adjacent grains for one another and reveal little as to the real properties of the metal itself.

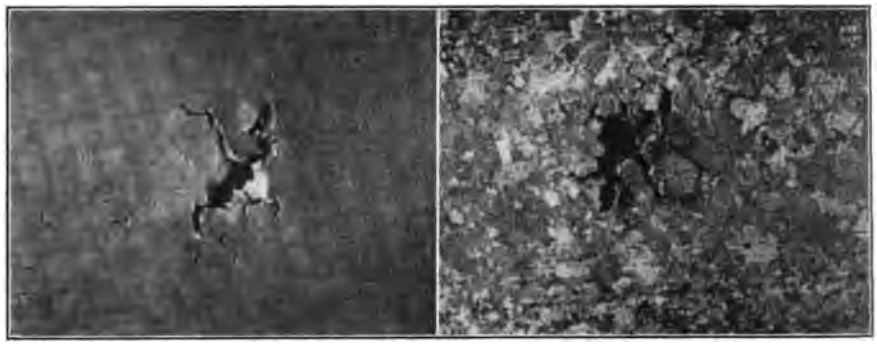
Even such a soft plastic substance as lead, under suitable conditions, may be rendered so weak and brittle that the metal can be easily crumbled into powder by the fingers although the constituent grains have lost none of the intrinsic properties of lead. Various erroneous explanations of this behavior of lead have appeared in the scientific literature, the change being described usually as an allotropic one. The importance, in an industrial sense, of a proper explanation of this type of the corrosion of lead justifies the description of the type of metal deterioration that follows.

Corroded Lead Sheathing

In Figs. 1 and 2 are shown two typical specimens of corroded lead sheathing selected from materials submitted to the Bureau of Standards for examination. Fig. 1 shows a section of the sheathing of an aerial cable; Fig. 2, that of the lead covering of a subterranean feeder-line of an electric light system. In this case the deterioration had proceeded to a much greater extent than in the case shown in Fig. 1 so that certain portions of the metal could easily be crumbled into a coarse gray powder by the fingers. This was particularly true of those portions of the sheathing

* Physicist, Bureau of Standards.

where surface discoloration showed it to have been immersed in water. The surface appearance of the embrittled lead is shown in Fig. 3. The sheathing in such spots was so weak and brittle that it could be easily crumbled into a gray powder although the appearance of the original surface was but little changed. In Fig. 4(*a*) some of the particles of the embrittled lead are shown, many of which are of a definite crystalline form. Each particle, when tested on a glass plate with a small pestle,



a. UNETCHED, SURFACE VIEW. × 3. *b*. SAME MATERIAL, ETCHED WITH CONCENTRATED NITRIC ACID. × 3.

FIG. 1.—INTERCRYSTALLINE BRITTLENESS IN COMMERCIAL LEAD. PART OF COVERING OF AERIAL CABLE; DETAILS OF SERVICE NOT REPORTED, OTHER THAN THAT IT OCCURRED IN A HOT CLIMATE. BREAK MAY HAVE BEEN RESULT OF COMBINED EFFECT OF STRESS AND CORROSION.

showed that it was very malleable and, when cut, the characteristic color of lead was revealed. That the lead is still malleable was illustrated by rolling portions of the embrittled lead into thin strips. By suitable care the metal was rolled as thin as 0.008 in. (0.2 mm.); the metal tears badly, however, during the rolling, as shown in Fig. 4(*b*). Evidently the coherence of crystals comprising the lead sheathing for one another had been greatly weakened but the crystals themselves still retained the characteristic properties of lead.

In Fig. 5 is shown the appearance of a cross-section of the sheathing. This was taken from a portion in which the metal was only partly embrittled. That the method of the corrosive attack is intercrystalline in its nature and that the action begins on the outer, or exposed, surface of the sheathing and proceeds inwardly, are very evident.

A chemical analysis of the material showed that there was no essential difference between the corroded and the uncorroded parts and that the lead contained a considerable amount of tin. A determination of the melting point of the material confirmed the indications of the chemical

FIG. 2.—CORRODED LEAD-CABLE SHEATHING. PORTION OF EMBRITTLED CABLE SHEATHING WAS FLATTENED OUT. PHOTOGRAPH SHOWS EXTERIOR OF SHEATH; SURFACE HAS BEEN BROKEN UP BY A NETWORK OF "ALLIGATOR CRACKS." THE METAL CAN BE EASILY CRUMBLED WITH THE FINGERS. ½ NATURAL SIZE.

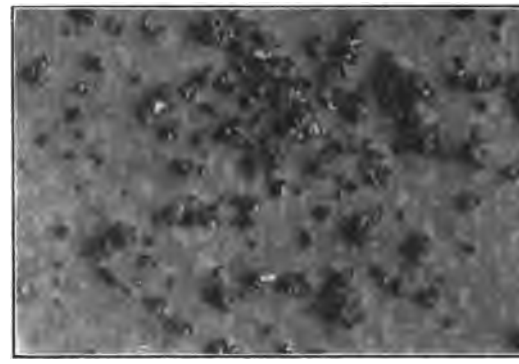
FIG. 3.—CORRODED LEAD-CABLE SHEATHING. SMALL GRANULAR SPOT IN FIG. 2 IS HERE SHOWN AT A HIGHER MAGNIFICATION. ROUGH CRYSTALLINE APPEARANCE OF THE METAL IS VERY EVIDENT. × 8.

analysis that the embrittled parts of the lead are essentially the same as the unattacked parts. These data are summarized in Table 1.

TABLE 1.—*Composition and Melting Point of Embrittled Lead*

	EMBRITTLED PORTION	UNATTACKED PORTION
Tin, per cent	1.09	1.06
Lead, per cent	98.3	98.28
Melting point, degrees C.	325.4	325.6

The melting point of pure lead is 327.4° C. (621.3° F.).



(*a*)

(*b*)

FIG. 4.—CORRODED LEAD-CABLE SHEATHING. (*a*) THE CORRODED METAL CAN BE EASILY CRUMBLED INTO SMALL GRAINS AS SHOWN. MANY OF THE GRAINS SHOW DEFINITE CRYSTALLINE FACES. × 8.

(*b*) GRAINS COMPOSING EMBRITTLED LEAD ARE STILL MALLEABLE. PIECES CAN BE ROLLED INTO THIN SHEETS IF CARE IS TAKEN. STRIPS TEAR BADLY IN ROLLING, HOWEVER. ABOVE STRIP WAS REDUCED FROM 0.12 TO 0.008 IN. IN THICKNESS. × 1

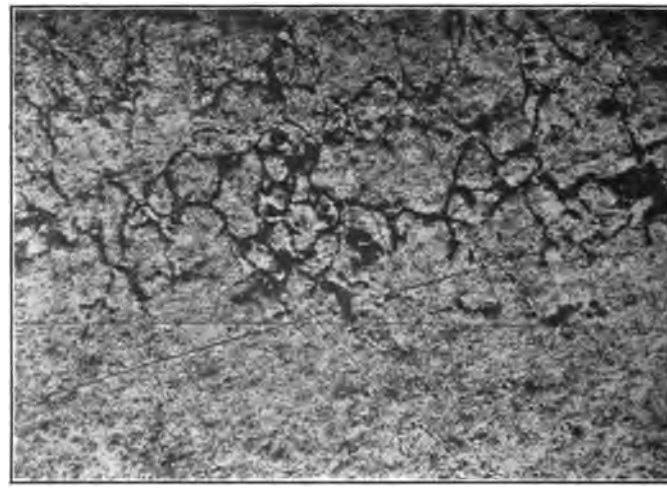


FIG. 5.—CORRODED LEAD SHEATHING. CROSS-SECTION THROUGH PORTION OF MATERIAL OF FIG. 2, WHICH WAS ONLY PARTLY EMBRITTLED. ACTION BEGINS AT OUTSIDE AND INTERCRYSTALLINE METAL IS FIRST ATTACKED. SPECIMEN IS UNETCHED. × 50.

The Allotropism of Lead

An allotropic form of lead similar in its properties to the well-known gray-tin has been described by Heller;[1] Creighton[2] has described an entirely different method by which this gray-lead appeared to be produced. In brief, Heller's method consisted in the immersion of bright sheets of lead in solutions of lead acetate which contained appreciable amounts of nitric acid. The transition was stated to have begun at the end of two days and to have been complete in about three weeks. The lead lost its original strength and ductility and disintegrated into particles, gray to gray-black in color, which could be pressed easily between the fingers into a pulverulent mass. The change was stated to occur to a very slight extent in lead immersed in solutions of pure lead acetate. The addition of a small amount of nitric acid, however, increased the rate of change very markedly. Lead solutions other than that of the acetate were found to permit the change to occur, but a small amount of nitric acid appeared to be necessary in every case. The inoculation of pure sheet lead with some of the "gray" form did not lead to any detectable change in the inoculated specimen. The lead used throughout the experiments was described as not containing "other metals in amounts worth mentioning. Neither silver nor tin was present and a trace, only, of iron was found."

The method described by Creighton consisted in the electrolysis of lead in nitric acid (sp. gr. 1.42), the lead being the cathode. The cathode was described as having increased slightly in volume and having lost its former malleability and firmness. The lower portion was found to have been completely changed. Small particles could easily be detached which could be rubbed into a fine powder or pressed together into a soft mass. Cohen and Helderman[3] have noted changes in the density of clean lead filings immersed for about three weeks in a lead acetate solution and have interpreted the density changes as evidence of an allotropic change occurring within the lead. An immersion of three weeks caused an increase in density from 11.322 to 11.342. Heating the lead after immersion has the effect of slightly lowering the density. These changes are, however, very much less in magnitude than those described by Heller and by Creighton.

Experimental Embrittlement of Lead

The methods described by Heller and Creighton by which the allotropic forms of lead may be produced were tested out for the purpose of

[1] Hans Heller: *Zeit. phys. Chem.* (1915) **89**, 761.

[2] H. J. M. Creighton: *Jnl.* Am. Chem. Soc. (1915) **37**, 2064.

[3] E. Cohen and W. D. Helderman: *Verslag* K. Akad. Wetenschappen (1914) **23**, 754–61.

comparison of the granular lead which may result from corrosion during service with the allotropic form.

In the description of the method given by Heller, lead-acetate solutions were used for most of the immersions, as was also done by Cohen and Helderman. In the preliminary trials, a solution similar to that described by Heller was used; water, 1000 cu. cm.; lead acetate, 400 gm.; nitric acid (sp. gr. 1.16), 100 cu. cm. In most of the experiments, however, normal solutions of neutral lead acetate were used and the concentration of nitric acid was varied in different tests from 0.5N to 2N. Two types of lead were used; a commercial lead of ordinary grade, and one pure lead of exceptionally high purity. The composition of the two grades is given in Table 2.

TABLE 2.—*Composition of Lead Used**

	Commercial Lead, Per Cent.	High-grade Lead, Per Cent.†		Commercial Lead, Per Cent.	High-grade Lead, Per Cent.†
Antimony	0.07	0.003	Zinc	Not detected	Not detected.
Iron	0.02	0.004	Bismuth		Not detected
Tin	0.14	Not detected	Silver		Not detected
Copper	Not detected	Not detected	Lead	99.72	99.993 (by difference)
Nickel	Not detected	Not detected			

* The author is indebted to Mr. J. A. Scherrer of the Bureau of Standards for these analyses as well as for the succeeding one.

† The analysis was carried out upon a sample of 100 g.

In the series of tests described below, thin sheets of pure lead 2 cm. by 4 cm. by 1.5 mm. were immersed in the different solutions for 24 days. Before use, the lead was annealed for approximately 3 hr. at 200° C. after it had been rolled into sheets to relieve any internal stresses, set up by the cold rolling of the material, that might influence the behavior of the lead when immersed in the electrolyte.

The following solutions were used, the specimens were suspended vertically by a silk thread, so as to be exposed to the solution on all sides.

No. 1. N lead acetate, 2N nitric acid
No. 2. N lead acetate, 1.6N nitric acid
No. 3. N lead acetate, 0.8N nitric acid
No. 4. N lead acetate, 0.5N nitric acid
No. 5. N lead acetate, no nitric acid
No. 6. N lead acetate, 1.6N nitric acid

Commercial sheet was immersed in solution No. 6, pure lead in each of the others; 50 cu. cm. of solution was used for each specimen. In all cases in which nitric acid was used a slight evolution of gas occurred,

particularly in the first part of the test period. This was identified as nitric oxide. The evolution of the gas from the pure lead immersed in solution No. 2 was at the approximate rate of 20 cu. cm. in 24 hr. When the commercial lead was immersed, the evolution was considerably faster. With solutions containing less nitric acid, the evolution of gas was progressively less as the concentration of the acid was decreased. It could

FIG. 6.—LEAD IMMERSED IN NITRIC-ACID SOLUTIONS OF LEAD ACETATE FOR 24 DAYS. SPECIMEN 1, PURE LEAD IMMERSED IN N SOLUTION OF LEAD ACETATE 2 N NITRIC ACID.

SPECIMEN 2, PURE LEAD IMMERSED IN N SOLUTION OF LEAD ACETATE 1.6 N NITRIC ACID.

SPECIMEN 3, PURE LEAD IMMERSED IN N SOLUTION OF LEAD ACETATE 0.8N NITRIC ACID.

SPECIMEN 4, PURE LEAD IMMERSED IN N SOLUTION OF LEAD ACETATE 0.5 N NITRIC ACID.

SPECIMEN 5, PURE LEAD IMMERSED IN N SOLUTION OF LEAD ACETATE.

SPECIMEN 6, COMMERCIAL LEAD IMMERSED IN N SOLUTION OF LEAD ACETATE 1.6N NITRIC ACID.

ALL ARE SLIGHTLY LARGER THAN NATURAL SIZE.

hardly be detected in the 0.5N nitric-acid solution and none whatever was observed in the solution of lead acetate to which no acid had been added.

A slight deposit or sludge formed in the bottom of the flask as the action of the solution upon the lead proceeded. In the cases where pure lead was used, the amount was very small and increased in amount as the concentration of acid increased. In the case of the commercial lead

the deterioration was more rapid and a relatively large amount of sludge formed. Pure lead immersed in solution No. 2 gave 0.02 gm. deposit after 5 days (of 24 hr. each) immersion while commercial lead in the

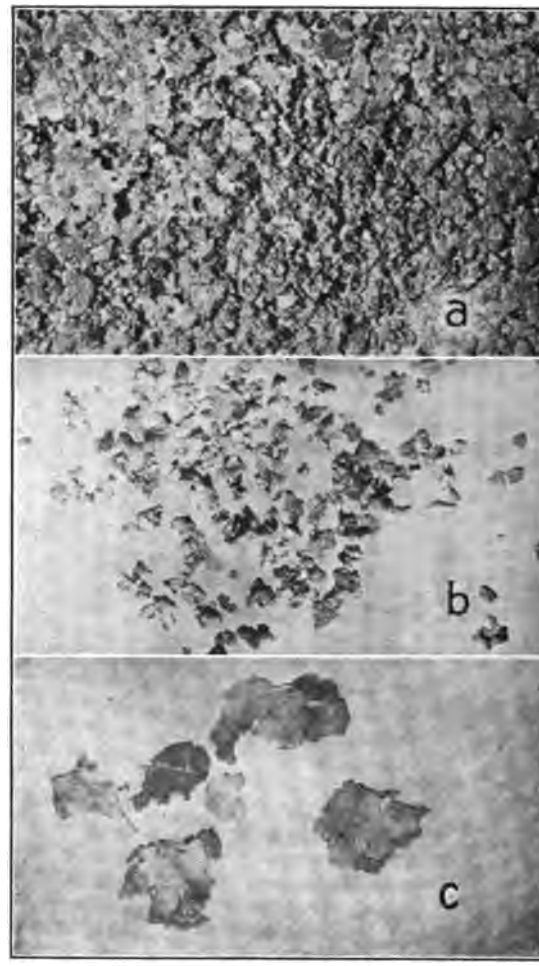


FIG. 7.—EMBRITTLED COMMERCIAL-LEAD SHEATHING. STRIP OF COMMERCIAL LEAD WAS IMMERSED IN A SOLUTION OF 1000 CU. CM. WATER, 400 GM. LEAD ACETATE AND 100 CU. CM. CONCENTRATED NITRIC ACID FOUR DAYS (96 HOURS):
(*a*) SURFACE VIEW OF SPECIMEN. × 8.
(*b*) CRYSTALS WHICH BECAME DETACHED AND FORMED SLUDGE ON BOTTOM OF FLASK. × 8.
(*c*) CRYSTALS SIMILAR TO THOSE OF (*b*) THAT HAVE BEEN FLATTENED. CRYSTALS STILL SHOW CHARACTERISTIC PROPERTIES OF LEAD. × 8.

same solution produced 0.52 gm. in the same time. The sludge produced from the commercial lead contained some rather large particles similar to those shown in Fig. 4(*a*), which were malleable and could be flattened

out on a sheet of glass, see Fig. 7, *b* and *c*. The solution continued to act upon these particles, as was indicated by the evolution of the gas,

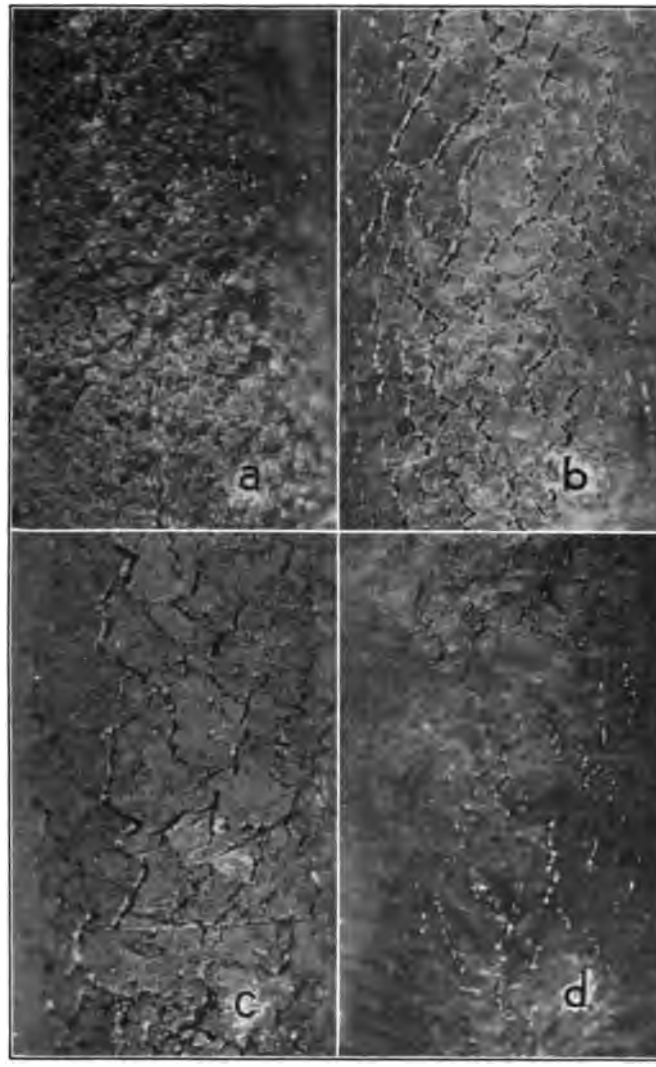


FIG. 8.—INTERCRYSTALLINE BRITTLENESS INDUCED IN PURE LEAD BY IMMERSION IN NITRO-ACID SOLUTION OF LEAD ACETATE.
(*a*) SPECIMEN 2, FIG. 6.
(*b*) SPECIMEN 3, FIG. 6.
(*c*) SPECIMEN 4, FIG. 6.
(*d*) SPECIMEN 5. FIG. 6.
ALL HAVE BEEN BENT AT AN ANGLE OF APPROXIMATELY 150° TO REVEAL INTERCRYSTALLINE WEAKNESS.

and finally only a gray flocculent powder remained. The sludge formed from the pure lead was of a flocculent nature and gray in color. This

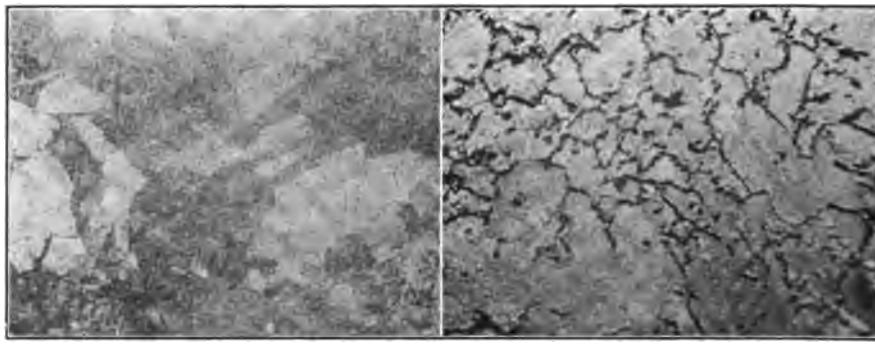
is evidently an oxidation product. It is well known that bright lead soon changes its color in water solution by oxidation, particularly if a trace of acid is present.[4]

(*a*) (*b*)

FIG. 9.—PURE LEAD SHOWING INTERCRYSTALLINE EMBRITTLEMENT. SHEET OF PURE LEAD WAS IMMERSED IN A SOLUTION OF N LEAD ACETATE, AND 0.5N NITRIC ACID, FOR 10 DAYS.

(*a*) SURFACE VIEW OF SPECIMEN AFTER RUBBING TO REMOVE SLIGHT "BLOOM" OR DEPOSIT; UNETCHED. × 15.

(*b*) SAME SPECIMEN AFTER BENDING THROUGH 150°. FISSURES REVEALED ARE TRULY INTERCRYSTALLINE. × 15.



(*a*) (*b*)

FIG. 10.—PURE LEAD SHOWING INTERCRYSTALLINE EMBRITTLEMENT. A SHEET OF PURE LEAD WAS IMMERSED IN A SOLUTION OF N LEAD ACETATE AND 1.6N NITRIC ACID FOR 12 DAYS.

(*a*) SPECIMEN AFTER A FEW MINUTES' IMMERSION. × 8.

(*b*) SAME SPECIMEN AFTER 12 DAYS' IMMERSION. AREA SHOWN IS NOT THE SAME AS THAT OF (*a*). CONSPICUOUS FISSURES HAVE FORMED AROUND MOST CRYSTALS. × 15.

The solutions in which the lead specimens were immersed gradually turned from colorless to a lemon color, the intensity of the color being proportional to the concentration of the acid initially present. At the end of the 24-day period during which the specimens were under obser-

[4] W. Vaubel: *Zeit. angew. Chem.* (1912) **25**, 2300.

vation, it was a simple matter to place the solutions in correct order with respect to the initial acid concentration by the color of the liquid; no change of color could be detected in the simple lead-acetate solution.

The appearance of the specimens at the end of the 24-day immersion is shown in Fig. 6. The specimens that were in the solutions of the greatest acid concentration were very much roughened and embrittled; those in the solutions of less acid concentration merely showed evidence of etching on the surface by which the crystalline structure was revealed. In some cases (Nos. 3 and 4), the action had been somewhat greater at the sharp corners and edges so that a rough crystalline appearance was produced at such points.

With specimen No. 4 (immersed in 0.5N acid), a very faint etch-pattern on one side of the sheet only was observed, the remainder still showed the marks due to rolling. The specimen immersed in the solution of lead acetate containing no acid showed no evidence of etching; the surface here, as in the other cases, was covered with a slight gray "bloom" which could be easily wiped off. Slight traces of "lead trees" at the sharp corners of the specimens were noted in one case of immersion in lead acetate.

The behavior of the different sheets, when bent sharply, indicates clearly that a more profound change occurred in the material than was indicated by the appearance of the surface. This is shown in Fig. 8. In each case, including those specimens, the surface appearance of which appeared to be suggestive of no appreciable change, the metal cracked and revealed a series of intercrystalline breaks, thus indicating that an intercrystalline brittleness of the lead had resulted from the action of the electrolyte. These intercrystalline breaks are best revealed in specimens immersed in lead-acetate solutions containing little or no acid. In the solutions of higher acid concentration, the attack of the metal along the crystalline boundaries is great enough so that the specimen is merely roughened. The preferential attack of lead along the crystalline boundaries during immersion in a solution of N lead acetate and 0.5N nitric acid for 10 days is shown in Fig. 9. The surface has the appearance of being very slightly etched; upon bending, however, wide fissures formed between the crystals parallel to the direction of bending. The more rapid attack along the crystal boundaries of metal immersed in solutions of high-acid concentration is shown in Fig. 10. The lead was immersed for 12 days in a solution of N lead acetate and 1.6N nitric acid. The results of the immersion of the lead in lead-acetate solutions are summarized in Table 3.

A number of attempts were made to produce the spongy lead, noted by Creighton, by means of electrolysis in concentrated nitric acid (sp. gr. 1.42). The lead used was the high-grade material listed in Table 2. This was made the cathode of the electrolytic cell, platinum foil being the

TABLE 3.—*Effect of Nitric-acid Solution of Lead Acetate upon Lead after 24-Days' Immersion*

No.	Type of Lead[a]	Solution, Concentrate of Nitric Acid in N Solution of Lead Acetate	Evolution of Gas	Color of Solution	Amount of Sludge	Character of Surface[b]	Behavior upon Bending[c]
1	Very pure	2N	Fine bubbles appear within a few minutes.	Deep lemon yellow.	Considerable deposit, about one-fifth of specimen had disintegrated.	Very rough.	Easily broke upon bending.
2	Very pure	1.6N	Fine bubbles appear within a few minutes.	Lemon yellow	Slight deposit (0.02 g. in 5 days).	Rough, a brittle layer formed on each side.	Deep continuous cracks formed.
3	Very pure	0.8N	A few very fine bubbles after several hours immersion.	Light lemon yellow.	Only a few isolated specks.	Surface was etched enough to show crystalline structure. The corners and edges were much roughened.	Short wide intercrystalline fissures opened.
4	Very pure	0.5N	Very small isolated bubbles seen occasionally.	A slight tinge of yellow could just be detected.	None.	Slight bloom on surface, faint etch markings visible.	Fine intercrystalline cracks were opened
5	Very pure	None	No bubbles detected.	Colorless.	None.	Slight bloom on surface, no evidence of etching.	Fine intercrystalline fissures opened.
6	Commercial	1.6N	Bubbles occurred within less than 1 min. after immersion.	Like No. 1.	Most of the specimen had disintegrated into sludge.	Only a few fragments of the specimen were left. Most of it was in the form of sludge	

[a] See Table 2 for composition. [b] See Fig. 6. [c] See Fig. 8.

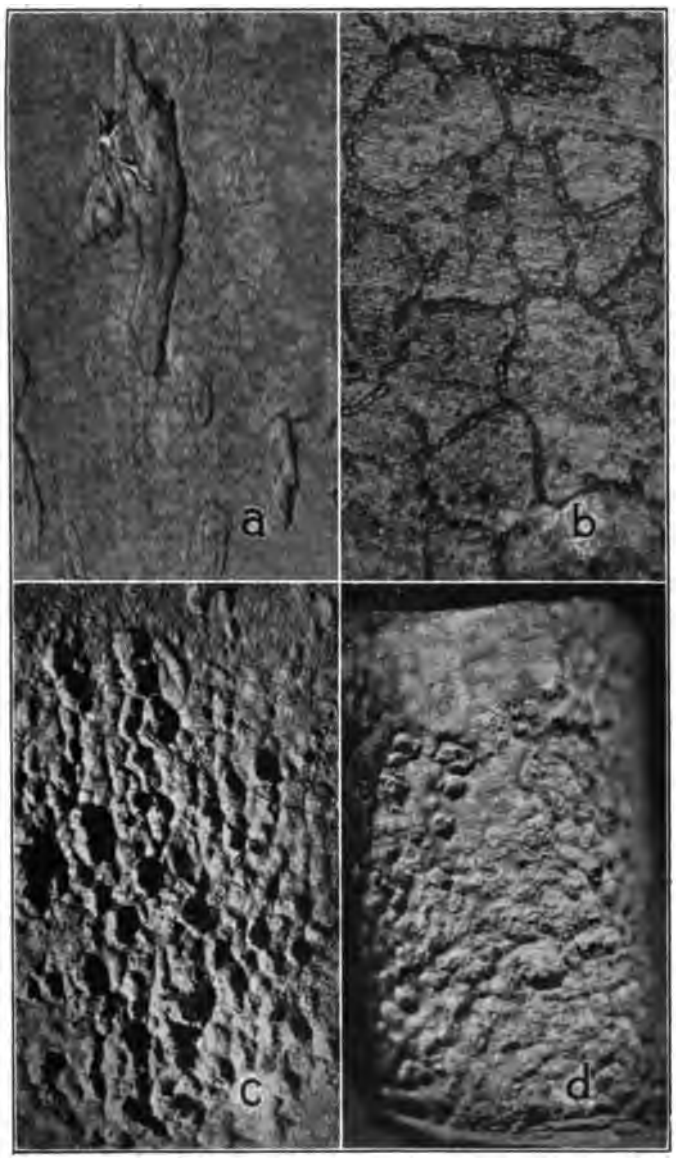


FIG. 11.—PURE LEAD USED AS CATHODE IN ELECTROLYSIS OF CONCENTRATED NITRIC ACID.

(*a*) SURFACE VIEW OF LEAD CATHODE AFTER 12 HOURS' TREATMENT; PORTIONS OF SPECIMEN SHOWED A DISTINCT INTERCRYSTALLINE ATTACK. × 9.

(*b*) SAME MATERIAL AS (*a*). INTERCRYSTALLINE NATURE OF ATTACK IS VERY EVIDENT HERE. × 50.

(*c*) SAME MATERIAL AFTER 36 HOURS' TREATMENT. NATURE OF SURFACE SUGGESTS THAT CRYSTALS ARE BODILY DISSOLVED AFTER INTERCRYSTALLINE ATTACK HAS STARTED. × 4.

(*d*) SAME MATERIAL AS (*c*), BENT AT AN ANGLE OF 180° C. METAL HAS NOT BEEN EMBRITTLED BY ELECTROLYTIC ACTION TO ANY APPRECIABLE EXTENT. × 4.

anode. The lead electrode was approximately 4 cm. by 1 cm. by 3 mm., a current of 2 amp. was used in most cases, although in some this was increased up to 3 amp. In most cases 50 cu. cm. of electrolyte was used.

A copious evolution of gas occurred at the platinum anode when the circuit was closed; this was a colorless gas but turned brown when air was admitted into a tube of it. Evidently it was nitric oxide. A fine stream of minute gas bubbles was also to be seen rising from the lead cathode. This gas, apparently, dissolves in the concentrated acid. Attempts were made to collect it in a test tube filled with concentrated nitric acid inverted over the cathode. No gas was collected, however, until the action had continued for more than 48 hr. and the color of the acid within the inverted tube had changed to a dark green. The gas, as collected, was dark brown in color and evidently was nitrogen peroxide. A white crystalline substance formed on the lead cathode, lead nitrate; this substance is rather insoluble in the concentrated nitric acid and collected as a heavy deposit on the cathode and on the bottom of the flask under this electrode.

When the action was allowed to continue for some time (24 hr.), a black gritty deposit formed upon the platinum electrode. This deposit usually formed after the solution had become rather warm and had evaporated considerably. This was the only substance formed that might be mistaken for an allotropic form of lead. In one case, when the solution evaporated to a very small volume, some of this black deposit was found on the lead cathode as well as on the platinum anode. All attempts to reproduce this condition, however, failed.

Chemical analysis showed that the black anode deposit was an oxide of lead. An oxygen content of 12.95 per cent. was found pure; lead peroxide, PbO_2, contains 13.35 per cent. oxygen. It is evident that the electrolysis of concentrated nitric acid is complicated by several secondary reactions. The production of nitrogen peroxide at the lead cathode and the lead peroxide at the anode are instances. Examination of the lead cathodes after the action was completed failed to show any pronounced embrittlement of the lead. Examination at intervals during the progress of the action showed that the attack of the metal often was intercrystalline in its nature. This is illustrated in Fig. 11, which shows the surface of the lead cathode at two different stages. The more rapid attack along the crystal boundaries is very evident. That the lead has not been rendered brittle by the electrolytic action is evident upon sharply bending the sheet, as in (*a*).

Explanation of Results

Most of the impurities that occur in lead are insoluble in the metal. This is true particularly of copper, zinc, iron, nickel, aluminum, and cobalt, which are only slightly miscible even when both metals are in the liquid state. Such impurities, after solidification, will be lodged between

the grains of the lead. Tin, antimony, and silver are completely miscible in lead in the molten state, but almost entirely insoluble in the solid state, with the exception of tin. Each of these three elements forms a eutectic series with lead. These, too, will occur between the grains of the metallic lead.

The difference in solubility of these impurities and of the pure lead comprising the interior of the crystal accounts largely for the disintegration of the metal by intercrystalline embrittlement when immersed in a weak acid solution. The greater rate of disintegration of the commercial lead, as compared with the pure lead, is due to the larger amount of these intercrystalline impurities. The greater solubility of the intercrystalline film of the lead-tin eutectic which must exist in the metal of corroded cable sheath (Fig. 2) as compared with that of the lead itself accounts for the rapid disintegration of this material when immersed in a solution consisting of substances leached out of the surrounding concrete.

It is to be concluded from the results of the experiments made that the so-called allotropic, or gray, lead described by Heller represented only a granular condition of the ordinary form of lead, the granulation having been brought about by the action of the electrolyte used, primarily the nitric acid, upon the intercrystalline impurities. No evidence of allotropy could be obtained in the experiments upon very pure lead carried out in the manner described by Heller, although unmistakable evidence of intercrystalline brittleness was secured. The attack of the intercrystalline metal in the high-grade lead by solutions of neutral lead acetate is in all probability to be partly ascribed to the difference in the electrolytic solution potential of the amorphous intercrystalline cement as compared with the metal of the interior. To this is to be added the effect of the slight intercrystalline impurities. The precipitation of lead from the solution in the form of "lead trees" in such experiments may be taken as one line of evidence. The change in density of lead specimens immersed in lead-acetate solutions, noted by Cohen and Heldeman, may be ascribed to an accompanying oxidation along the grain boundaries, such as readily occurs in water or weak aqueous solutions on freshly exposed surfaces of lead. This explanation does not completely account for all the changes in density noted, however. No evidence of embrittlement by means of electrolysis could be obtained, nor was any product formed, other than a deposit of lead peroxide upon the anode, which might be mistaken for an allotropic form of lead. It is to be concluded that the forms previously described as allotropic lead were only a granular condition of the ordinary form brought about by intercrystalline embrittlement, accompanied perhaps by slight oxidation.

SUMMARY

1. A type of deterioration of lead that renders the metal weak, brittle and capable of being crumbled easily into grains is described. The deterioration occurs as a result of corrosion during service; the attack of the metal is localized along the crystal boundaries and the brittleness produced is truly intercrystalline in its nature.

2. Practically all of the commonly occurring impurities in lead are insoluble in the solid state and are to be found lodged between the grains of the lead. The intercrystalline brittleness is due largely to the behavior of these impurities when the metal is immersed in an electrolyte.

3. Specimens of very pure lead were treated in the manner described by previous investigators for the production of the allotropic form of lead. No evidence was obtained to justify the claim that lead may exist in an allotropic state analogous to the well-known gray tin.

4. The forms of lead previously described in the scientific literature as allotropic states appear to be due to an intercrystalline attack by the electrolyte, immersion in which was necessary to bring about the allotropic change. The rate at which the so-called allotropic transformation occurs is largely a function of the purity of the lead and the acidity of the electrolyte in which the metal is immersed.

The author wishes to acknowledge the very efficient help of Mr. J. F. T. Berliner in the many examinations necessary in the course of the investigation.

DISCUSSION

(*Includes also the paper by Messrs. Rawdon and Langdon, p.* 439)

J. W. RICHARDS,* Bethlehem, Pa.—I am greatly interested in the electrolytic features of the attack on the lead, and the conclusions are apparently unimpeachable. One phenomenon that occurs when lead is used as a cathode, however, is not mentioned, though it may have some relation to this problem. When lead is used as a cathode with a high current density in alkaline solution, there is an extremely fine dusting of lead; this dusting is usually ascribed to the formation of a lead-sodium alloy on the surface of the lead, the attack of which by the solution gives molecularly divided lead. The lead is so finely divided that it forms a liquid that looks like ink; it takes about half a day to settle.

I made use of this phenomenon in assaying sea-water for gold. This fine lead dust absorbs the gold and silver in the sea-water, which can later be filtered out. The lead is then assayed to get the silver and gold, so as to determine the amount that is in the liquid used. In that way, I have determined the amount of silver and gold in 1 c.c. of sea-water.

* Professor of Metallurgy, Lehigh University.

but found that this method of recovering the metals would cost just about the value of the gold and silver obtained.

The explanation that the material between the crystals, the eutectic, is attacked is, from the electrochemical standpoint, very plain. It is undoubtedly true that the purer metal is less attackable than the eutectic between the crystals, so that local circuits are formed which precipitate little crystals of lead upon the metallic crystals.

ZAY JEFFRIES,* Cleveland, Ohio.—In England, recently, considerable attention has been given to the study of intercrystalline brittleness in lead and other metals, especially brass, particularly by Rosenhain, Archbutt, Hanson, and Hatfield. Rosenhain and Archbutt have explained season cracking in ordinary rolled brass, which is known to be an intercrystalline failure, by the assumption that the intercrystalline material is amorphous and that its rate of deformation with an applied load is entirely different from that of the crystalline material. They have also obtained the same results with lead of great purity. In other words, according to their theories, lead does not have to be impure to show this intercrystalline brittleness. The explanation accords with the amorphous theory very nicely; the amorphous phase of lead is viscous, it deforms slowly with load; the crystalline phase is not viscous and does not deform permanently until a certain load is applied, when it deforms quickly to a certain predetermined amount, according to the load, and then its deformation ceases. The amorphous metal is like pitch; it deforms gradually and eventually breaks. They report the same thing in connection with boiler plate under stress at a temperature of 200° to 400° C.; they find that the long exposure to load produces intercrystalline brittleness.

Intercrystalline brittleness may, however, be due to many things. Doctor Merica's paper some years ago showed that the beta phase at the grain boundaries in alpha-beta brass produced intercrystalline brittleness probably because of a difference in coefficient of expansion. The intercrystalline brittleness of tungsten may be due to the difference in coefficient of expansion of the amorphous and crystalline phases alone. The intercrystalline brittleness due to brittle eutectics, such as bismuth and gold, is well known.

There is also intercrystalline brittleness due to the difference in specific properties of the amorphous and crystalline phases, which is usually found at relatively high temperatures in any metal. For example, we will get intercrystalline brittleness in iron, at a temperature of yellow heat, with long application of the load. We get intercrystalline fracture of copper at high temperature; in fact, nearly all of the metals, if loaded slowly, at high temperatures will break at the grain boundaries.

* Director of Research, Aluminum Castings Co.

This type of intercrystalline fracture is supposedly due to the soft amorphous phase, which simply pulls apart and leaves the crystals intact On the other hand, tungsten will break at the grain boundaries at very high temperatures; on cooling to an intermediate temperature, it will break through the grains; and at room temperature, it will again break in the grain boundaries. It is thus seen that there is no one cause for intercrystalline fracture; it behooves us to find the particular reasons for a given case.

G. H. CLAMER,* Philadelphia, Pa.—A certain phenomenon has been puzzling the scientific heads of our railroads for a great many years; namely, the linings of car bearings after a period of service start cracking. The reason for such cracking has usually been attributed to the impurity content.

Car-journal bearing linings, in the earlier days, were made of pure lead but in recent years the lead has been hardened with tin and antimony. The pure lead linings cracked as well as those made from the antimony, tin, and lead alloys, although not to the same extent numerically. No satisfactory explanation has been made to account for the cracking of the pure lead linings.

In such service, there are compressive strains and elevated temperatures, which might become excessive if the oil film is interfered with. As the lining is supported by tinning to the back, in the absence of an oil film, under the rolling action a tensile strain may be submitted to the lining. The linings crack, become loose, and fall out; hot boxes result, giving annoyance to the passengers and expense of operation.

F. A. HALL, Philadelphia, Pa.—The Wright-Martin Aircraft Corpn. had considerable trouble with the connecting-rod bearings, which consisted of a bronze shell with a babbitt lining containing 92 parts tin, 4 parts copper, and 4 parts antimony. These bearings failed in a similar manner to those described by Mr. Clamer. An investigation was being made when the Armistice was signed. A microscopic investigation revealed that the cracking of these babbitt linings was between the crystals; although at that time we did not attach any particular importance to this fact, as we were looking for impurities in the nature of included oxides. The Liberty engine had similar difficulties, and in so far as I have been able to learn, no real solution has been found for this trouble. It would seem that these failures are due to similar causes and each particular case is only a question of degree and not of kind.

J. W. RICHARDS.—The fundamental reason for some of these difficulties may be explained from the electrochemical standpoint. Place in an electrolyte two plates of different metal connected with a wire;

* First Vice-president and Secretary, Ajax Metal Co.

there is at once evidence that one is being attacked and that the other is not. The one being attacked acts as an anode and the other acts as a cathode. The current will run through the wire in one direction and through the electrolyte in the opposite direction. If the two plates are placed in contact with each other they are short-circuited; but one still acts as the anode and the other as the cathode. The current engendered, however, instead of going through the wire passes across the junction and the self-generated current passes through the solution.

Suppose that one of these plates is impure metal and that in it is a grain of pure lead. I have in mind the Pattinson process of concentrating pure lead crystals out of the lead-silver alloy, you are all familiar with that. When a solution containing lead and silver, let us say, is cooled, the pure lead crystals separate out, being less fusible than the eutectic, and then the eutectic solidifies, forming the mass between the grains of the lead.

If a grain of pure metal, like lead, is surrounded by some intercrystalline material, you have exactly these conditions: The pure lead is the cathode; the intercrystalline material, or the lead alloy, is the anode; and the current passes through the solution from the anode to the cathode. Every crystal of pure lead acts as a cathode and every bit of impurity acts as an anode. The local circuits take place through the electrolyte and the return current passes through this junction, where the particles are in metallic contact with each other. It is only where the metal is absolutely one thing and there is no heterogeneity that it is possible to avoid this local action; as soon as there is a differentiation, one material acts as the anode and another as the cathode.

Any particular case of corrosion might be investigated in the laboratory by using as one plate the very purest lead, or other metal, and as the other plate some of the alloys of definite composition, and measuring the voltage between them. The potential generated between the two would give an actual proof of the currents that must exist, in these local circuits, between the impurities and the crystals of pure metal. Alloys might be found that act as the cathode with the lead as anode, but in these cases the alloy will act as the anode and the pure crystals as the cathode, the pure metal being generally less attackable than the alloys.

T. D. YENSEN,* Pittsburgh, Pa.—Norman B. Pilling[5] has found that brittleness in slightly oxidized copper may be due to hydrogen, on account of the ease with which hydrogen diffuses through the copper at high temperatures, and the difficulty with which the resulting water vapor diffuses out.

Mr. Rawdon calls especial attention to the fact that the copper was slightly oxidized. Is it not possible that there may be some connection

* Research Engineer, Westinghouse Elec. & Mfg. Co. [5] *Trans.* (1919) **60**, 322.

between the brittleness found by Mr. Rawdon and that found by Mr. Pilling in his investigation?

J. W. RICHARDS.—Might I suggest that copper that has dissolved hydrogen, let us say, is another illustration of the same principle which I have explained; namely, that the copper hydrogen forms a eutectic; that as the mass sets, pure copper crystals will solidify from the eutectic at higher temperature than the copper-hydrogen eutectic. We all know the great chemical activity of the metal hydrogen couples. It is the basis of the use of nickel as a catalyzer in the hydrogenation of oil. Hydrogen thus dissolved in metal is far more active than free hydrogen; and therefore the copper-hydrogen eutectic would be chemically much more active than the pure copper crystals and might set up this disintegrating force.

F. L. ANTISELL,* Perth Amboy, N. J.—We have done some work along the lines outlined by Professor Richards and find that galvanic action will be established between electrodes of similar metal but dissimilar size. The physical state of the electrodes and their manipulation affect the value of the potential and polarity but do not change the fundamental phenomena when the electrodes are substantially different in size and with a given electrolyte.

If two copper electrodes, one having one-fourth the area of the other, are immersed in a dilute sulfuric-acid solution, the voltmeter will indicate a potential of, say, 30 millivolts. The smaller electrode will act as the cathode and the larger will act as the anode. If a copper-sulfate electrolyte is used, the polarity will be reversed, the larger electrode acting as the cathode and the smaller as the anode. The electromotive force is due to their dissimilar sizes and the polarity and potential are governed by the character of the electrolyte. The millivolt readings vary with the concentration of the sulfuric-acid and copper-sulfate solutions and, when plotted, give a curve showing positive and negative readings, the electrodes being kept the same.

If this curve is plotted on a four quadrant diagram, the upper ordinates represent the percentage of acid, and the lower ordinates the percentage of copper sulfate, the readings on the abscissa being positive to the right and negative to the left, the curve will run from the first quadrant through zero and into the third quadrant. With mixtures of sulfuric acid and copper sulfate, both negative and positive readings are obtained, depending on the concentration of the constituents. There is one combination at which zero potential exists; this, however, could not be obtained experimentally but only by drawing a smooth curve through the other points on the curve.

* Superintendent, Raritan Copper Works.

This indicates that there are, probably, some eutectics corresponding to solutions giving high millivolt readings and some that approach the zero-potential solution. This may be one explanation for the difference in the rapidity of deterioration of metals. Those having eutectics near the zero-potential condition will establish slight action, the potential being established by the dissimilar size of the grains in the matrix. Therefore, with a given eutectic, which is assumed to be the electrolyte, the local action will vary with the size of the grains. The annealing of a metal, rearranging the grains, decreases the intensity of the local action.

J. W. RICHARDS.—The statements just made ignore the fact that the electrolyte usually contains dissolved air, or oxygen, and that the larger plate is in contact with more oxygen than the smaller plate; also that the smaller plate has had more work put on it. The parts of a sheet of metal that have been worked the most, strained the most, will act as an anode toward the parts that have been strained the least; so that when the sheet is immersed in liquid, the parts that have been most strained, or most worked, will be corroded most.

The question of a greater amount of mechanical work making the material more susceptible to acting as an anode toward the unworked part and the gases in solution having some relation to the size of the plates illustrates how difficult it is to get two metals which, electrically, are exactly alike. It is practically impossible to get two pieces of metal that can be put into a given solution and not find that one is electropositive to the other. It is difficult to get evidence of a current flowing, which points to the universal occurrence of these little voltaic couples that arise under all sorts of conditions, of which just a few have been enumerated here, and which are the active factors in corrosion.

NORMAN B. PILLING, East Pittsburgh, Pa. (written discussion).—Messrs. Rawdon and Langdon have described the peculiar action that a bath of fused sodium chloride exerts upon copper annealed in it. The brittleness developed and the microstructural features accompanying the action bear a striking resemblance to the well-known destructive effects of hydrogen on oxygen-bearing copper. In view of the novel explanation suggested by the authors, *i.e.*, a galvanic action between the copper and the steel container resulting in the electrolysis of the fused salt and subsequent formation of a weak, penetrating, copper-sodium alloy, the writer has made a few experiments but has arrived at a different, although equally tentative, explanation.

He has not been able to confirm the necessity of an electrolytic environment in producing the action but has found that not only were anode and cathode equally affected but that simple immersion of the copper section (suspended by a copper wire) in the fused salt is sufficient

to bring it about. The invariable accompaniment of immersion in the fused salt is a peripheral deoxidation extending inward to a considerable depth. This has not been specifically mentioned by the authors but an examination of Fig. 3*a* is suggestive in this respect. It has been the writer's experience that the cuprous oxide distribution in copper is more clearly shown, after careful polishing, before etching than after. In the case of partly deoxidized copper, the Cu_2O particles are sufficiently hard to stand in clear relief; after etching, however, the distinction between oxygen-bearing and oxygen-free areas is more difficult to make on account of the development of obscuring crystalline detail and uncovering of small pits—covered during polishing—marking the site of former oxide particles.

FIG 12.—COPPER, 0.084 PER CENT. OXYGEN. NOT ETCHED. × 100.

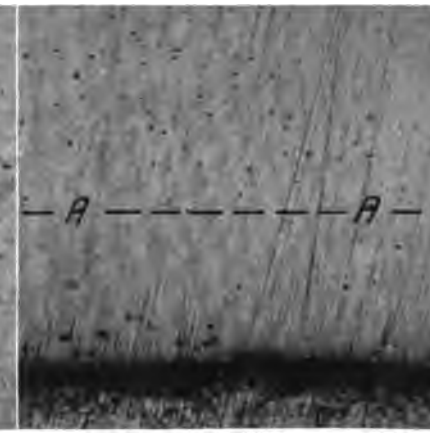


FIG. 13.—SAME, AFTER 15 MIN. IMMERSION IN FUSED SODIUM CHLORIDE. DEOXIDATION TO DEPTH A–A. NOT ETCHED. × 100.

This internal deoxidation requires a reducing agent soluble in solid copper at the annealing temperature and if it is assumed that molecular hydrogen (from gas flame, oily articles, etc.) may be dissolved in molten salt[6] a ready explanation is at hand. In this case one would have the usual splitting apart of the grains by the (relatively) insoluble water, formed by reduction of the cuprous oxide, and as this action is dynamic in nature, depending on a rapid accumulation of the former, the severity of the action would hinge on the hydrogen concentration.

A sodium-chloride bath melted in an oxidizing atmosphere is sufficiently reducing to show this effect. A quantity of c.p. sodium-chloride crystals were melted in small portions in an electrically heated, unglazed

[6] An assumption with some experimental support, according to recent unpublished work in this laboratory.

porcelain tube, previously heated 1 hr. in air at 900° C. Fig. 12 shows a section of a copper strap containing 0.084 per cent. oxygen; Fig. 13 is the edge of the same piece (mounted in solder) after 15 min. immersion in this salt bath at 900° C., showing deoxidation to the depth A–A (0.2 mm.), and a slightly fissured structure. A possible source of hydrogen in this case would be the dissociation of the water originally present in the salt crystals.

HENRY S. RAWDON (author's reply to discussion).—The note on the Intercrystalline Brittleness of Copper was offered as much for its suggestiveness as for any other reason. In view of the discussion brought out it seems to have answered its purpose.

The authors are of the opinion that the pronounced structural differences shown in Figs. 2 and 3 in Intercrystalline Brittleness of Copper are not fully accounted for by the tentative explanation suggested by Mr. reilling. The changes obtained were so pronounced and the chances for Pduction by hydrogen under the conditions of the experiment so slight that it appears that some cause must be sought to account for the embrittlement in addition to the well-recognized effect of hydrogen on copper. Whatever this cause may be, it is evident that an impressed e.m.f. was necessary to cause the pronounced change to occur. It should be noted that the rod used as anode remained remarkably free from anything suggesting brittleness, although the surface was attacked by the molten salt bath to a very appreciable extent.

The point that interests the authors as much as any concerning the subject of brittleness was brought out in the concluding paragraph, that is, the marked effect of a superficial brittle layer on the mechanical properties of the whole rod.

Charpy Impact Test as Applied to Aluminum Alloys

By E. H. Dix,* Jr., M. E., M. M. E., Cleveland, O.

(Columbus Meeting, October, 1920)

The success of the Charpy impact test in the steel industry has led those interested in aluminum alloys to investigate the possible application of this test to aluminum and its alloys. In this paper are set forth the results of a few preliminary tests made at the Lynite Laboratories of the Aluminum Manufactures, Inc. In order to study more thoroughly the significance of the Charpy test, slow-bending tests have been made duplicating the arrangement of the impact machine. Tests have been made on both notched and unnotched specimens of a series of copper-aluminum alloys.

Apparatus

The standard American-made Charpy impact machine delivering a blow of over 200 ft.-lb. was much too large to test aluminum-alloy specimens of the same type used for steel, so that it was necessary either to adopt a larger specimen or to have a special light-weight hammer made. Since there is no known relation between specimens of different sizes, even though geometrically similar, it was decided to adhere to the 10 by 10 mm. specimen. Accordingly, Sauveur and Boylston, the American makers of the machine, were asked to construct a special light-weight pendulum adapted to their standard machine, this pendulum to have one-tenth the capacity of the standard. The writer wishes here to acknowledge his indebtedness to Mr. H. M. Boylston for the personal interest and care exercised in constructing this pendulum.

The machine with the light-weight hammer in place is shown in Fig. 1. It is mounted on a concrete foundation with the concrete covering the flange on the base of the machine. Vibration is further prevented by four $\frac{5}{8}$-in. (15.8 mm.) foundation bolts. The large standard hammer shown against the wall was also used for some of the unnotched bars that required more than 20 ft.-lb. to rupture.

When the light-weight hammer was received, it was carefully cali-

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* Assistant Engineer of Tests, Lynite Laboratories, Aluminum Manufactures, Inc.

brated.[1] The center of percussion was found to lie within 0.11-in. (2.8 mm.) of the center of the specimen in place on the anvil, which in a length of 29.5 in. (74.9 cm.) is considered very good. Our determination of the radius to the center of gravity checked with the manufacturer's within 0.04-in. (1 mm.). The large hammer was also calibrated and found satisfactory. The complete data on the two hammers are:

FIG. 1.—CHARPY IMPACT MACHINE WITH LIGHT-WEIGHT HAMMER.

	STANDARD HAMMER	LIGHT-WEIGHT HAMMER
Capacity in foot-pounds	221.0	21.3
Weight, pounds	50.7	5.07
Radius to center of gravity, inches	26.88	26.02
Radius to center of specimen, inches	29.50	29.50
Radius to center of percussion, inches	30.17	29.39

The friction of the machine when using the large hammer need not be considered, but with the light hammer this friction must be taken care of. The total friction may be divided into three parts. (*a*) Bearing

[1] See E. H. Dix, Jr.: The Single Blow Notched Bar Impact Test as Used in the American Industry. *Proc.* Amer. Soc. Test. Mat. (1919).

and wind friction from release to point of impact; (*b*) bearing and wind friction from point of impact to high point of swing after fracturing the test piece; (*c*) needle friction from point of impact to high point after fracturing. Part (*a*) is practically constant for all tests, provided the bearings are kept clean and well oiled. Parts (*b*) and (*c*) are variable, depending on the energy absorbed by the test specimen. It was at first thought that these three parts of frictional loss could be easily calculated by allowing the pendulum to swing freely and noting the loss in height caused by each swing. This could be obtained both with and without needle friction. The difference between the two would, of course, give the needle friction part (*c*). Part (*a*) was assumed to be one-half the energy lost during the first swing. By taking readings of the friction loss from the time the pendulum was released until it came to rest, it was thought that we could obtain the friction of part (*b*) for any dial reading, this being assumed to be one-quarter of the loss caused by a double swing.

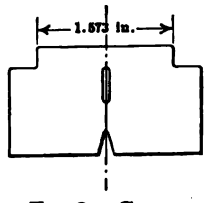


FIG. 2.—GAGE FOR CHECKING SPAN AND LOCATING KNIFE OF PENDULUM AND NOTCH OF SPECIMEN.

A great many determinations were made along these lines and a very careful and thorough study was made of the action of the pendulum, but it was found impossible to obtain satisfactory checks. All attempts to calculate the friction loss were, therefore, abandoned and another method of correcting for friction adopted. In this method, the angle to which the pointer is carried from its zero position when the pendulum is released was carefully measured on a number of different days. It was found that, with the bearings in good condition and the pointer properly adjusted, this angle was 159°. This reading is taken as the zero reading for all calculations and the difference between this angle and the angle to which the pendulum rises after fracturing a test piece gives the energy absorbed by the test piece. The span (40 mm. = 1.573 in.) was accurately checked by the gage shown in Fig. 2, which was also used for locating the knife of the pendulum and the notch of the specimen centrally.

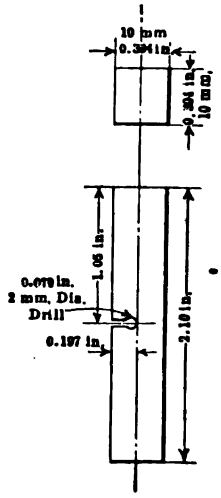
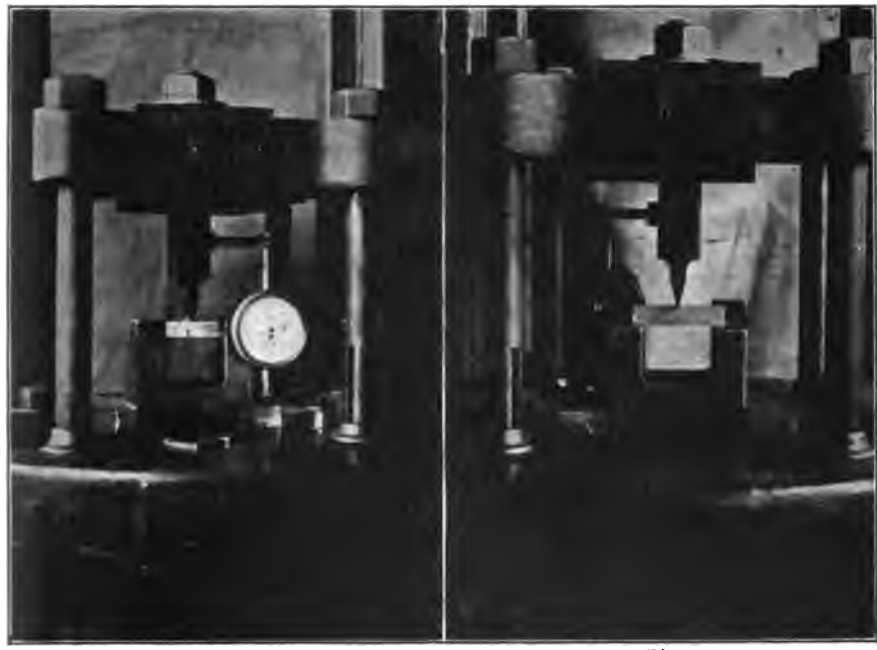


FIG. 3.—FORM AND DIMENSIONS OF TEST SPECIMENS.

It has been the experience of the writer that the particular type of notch selected is not nearly as important as the adoption of one standard and closely adhering to it. From the point of view of uniformity and ease of duplication, he has found the cylindrical notch used by the Bureau of Aircraft Production very satisfactory and has therefore used it in all of

this work. The dimensions of the specimen are shown in Fig. 3. The specimens were prepared by a pair of straddle mills and the notch was drilled by a 2-mm. drill accurately located by a jig. Tests were made on both notched and unnotched specimens of the same overall dimensions.

The set up for the slow-bending test is shown in a 10,000-lb. (4535-kg.) hand Olsen testing machine in Fig. 4. The knife-edge fixed in the moving head of the machine has the same contour as the Charpy knife. The steel block for supporting the specimen has the same span as the impact machine; this block was held rigidly in place by two pairs of wedges. The deflections were measured by an Ames dial. For the



(*a*) (*b*)

FIG. 4.—HAND OLSEN TESTING MACHINE. (*a*) FRONT VIEW OF SLOW-BENDING SET UP. (*b*) REAR VIEW OF SLOW-BENDING SET UP.

more ductile alloys, a dial having a travel of ¾ in. (19 mm.) and reading to 0.001 in. (0.025 mm.) was used, and for the more brittle, a dial of ¼ in. (6.35 mm.) travel reading to 0.0001 in. (0.0025 mm.). The testing machine was provided with a light-weight rider so that the capacity was 1000 lb. (453.5 kg.) and readings were made to 1 lb. (0.45 kg.) with ease. The testing machine had been previously calibrated and found accurate within 1 pound.

MATERIAL

The tests reported here were made on a series of copper-aluminum alloys (copper 0, 2, 4, 8, and 12 per cent.). Square bars 9/16 in. by 9/16 in.

by 9 in. long (1.4 by 1.4 by 23 cm.) were cast in sand, as shown in Fig. 6, each bar giving four impact specimens. A pouring temperature of 1300° F. (705° C.) in the ladle was used throughout. Standard 0.505 in. (12.8 mm.) tension bars were cast for comparison, as shown in

FIG. 5.—TENSION TEST BARS.

Fig. 5. One mold of Charpy bars (sixteen specimens) and two molds of tension bars (four specimens) were cast from each heat. The chemical analyses of these heats are shown in Table 15.

FIG. 6.—CHARPY IMPACT TEST BARS.

CONDUCT OF TESTS

The Charpy impact tests were made in the usual manner, the following data being taken: Height, thickness, thickness back of slot, length of specimen, dial reading, and condition of fracture. The specimen was set by means of the gage shown in Fig. 2. The impact resistance, in foot-pounds, was taken from a curve of dial reading plotted against impact resistance and was read to $\frac{1}{100}$ foot-pounds.

The slow-bending tests were made by taking simultaneous readings of load and deflection. After the yield point of the material had been reached. there was a giving of the specimen after the beam had been first

balanced; this was particularly true for pure aluminum. In general, readings were taken only after sufficient deformation had been applied so that the specimen would hold the load without noticeably giving. For the pure aluminum, this required from 3 to 5 min. for each reading. To show the effect of time in loading, one run was made by taking a reading of the load immediately the deformation was applied and then 10 min. later. The deformation was applied by hand at a slow rate. The readings of load, in pounds, were plotted against deflection at the center of the beam, in inches, the area under the curve representing the foot-pounds of energy required to fracture the specimen.

TABLE 1.—*Charpy Impact Results on Pure Aluminum (Lot 1821)*

Notched Bar			
Specimen No.	Ft.-lb.	Specimen No.	Ft.-lb.
A	9.85	G	9.27
B	7.61	H	9.29
C	9.70	I	7.20
D	9.90	J	8.75
E	7.80	Aver....	8.89
F	9.50		

TABLE 2.—*Charpy Impact Results on Pure Aluminum (Lot 1987)*

Notched Bar		Unnotched Bar*	
Specimen No.	Ft.-lb.	Specimen No.	Ft.-lb.
A	10.65	I	
B	10.45	J	50.5
C		K	42.6
D		L	35.0
Aver....	10.55	Aver....	42.7

Ratio of unnotched to notched, 4.05.

* Specimens broken with large hammer.

TABLE 3.—*Charpy Impact Results on 2 Per Cent. Cu-Al Alloy (Lot No. 1988)*

Notched Bar		Unnotched Bar*	
Specimen No.	Ft.-lb.	Specimen No.	Ft.-lb.
A-1	6.60	I	
B-1	6.05	J	19.3
C-1	4.65	K	25.3
D-1	4.26	L	17.0
Aver.....	5.39	Aver....	20.5

Ratio of unnotched to notched, 3.80.

* Specimens broken with large hammer.

TABLE 4.—*Charpy Impact Results on 4 Per Cent. Cu-Al Alloy (Lot No. 1989)*

Notched Bar		Unnotched Bar*	
Specimen No.	Ft.-lb.	Specimen No.	Ft.-lb.
A-1	1.99	I	8.14
B-1	2.01	J	6.85
C-1	1.60	K	9.58
D-1	1.50	L	9.29
Aver,...	1.78	Aver....	8.46

Ratio of unnotched to notched, 4.76.

TABLE 5.—*Charpy Impact Results on 8 Per Cent. Cu-Al Alloy (Lot No. 1990)*

Notched Bar		Unnotched Bar	
Specimen No.	Ft.-lb.	Specimen No.	Ft.-lb.
A	1.08	L	4.36
B	0.92	M	4.03
C	1.02	N	4.95
D	0.90	O	4.93
Aver.....	0.98	Aver....	4.57

Ratio of unnotched to notched, 4.66.

TABLE 6.—*Charpy Impact Results on 12 Per Cent. Cu-Al Alloy (Lot 1991)*

Notched Bar		Unnotched Bar	
Specimen No.	Ft.-lb.	Specimen No.	Ft.-lb.
A	0.76	I	1.65
B	0.57	J	2.13
C	1.10	K	1.85
D	0.68	L	1.97
Aver....	0.78	Aver....	1.90

Ratio unnotched to notched, 2.44.

TABLE 7.—*Slow-bending Results on Pure Aluminum Notched Bar (Lot 1821)*

Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.
K	202	0.93	5.54
*	185	0.93	5.24
L	224	1.13	6.11
M	254	0.90	7.33
N	242	1.13	6.14
O	262	0.85	9.23
Aver.....	227	0.98	6.87

Ratio to Charpy impact, 0.77.

* High reading taken instantaneously, low reading after 10-min. rest.

TABLE 8.—*Slow-bending Results on Pure Aluminum (Lot 1987)*

Notched Bar				Unnotched Bar			
Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.	Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.
E	244	1.08	6.85	M	700	1.00	33.95
F	250	1.06	8.82	N	658	0.85	28.55
G	250	1.09	7.53	O	650	0.95	27.30
H	236	1.13	6.53	P	666	1.10	40.60
*	204	1.13	5.80				
Aver.....	245	1.09	7.43	Aver.....	669	0.98	32.60

Ratio of foot-pounds unnotched to notched, 4.38. Ratio of maximum load of unnotched to notched, 2.73.

* High reading taken as soon as beam balanced, low taken after 5-min. rest and is not included in average.

TABLE 9.—*Slow-bending Results on 2 Per Cent. Cu-Al Alloy (Lot 1988)*

Notched Bar				Unnotched Bar			
Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.	Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.
A	250	0.45	4.37	E	939	0.55	15.66
B	310	0.60	6.59	F	1142	0.55	21.80
Aver.....	280	0.53	5.48	Aver.....	1040	0.55	18.73

Ratio of foot-pounds of unnotched to notched, 3.42. Ratio of maximum load of unnotched to notched, 3.72.

TABLE 10.—*Slow-bending Results on 4 Per Cent. Cu-Al Alloy (Lot 1989)*

Notched Bar				Unnotched Bar			
Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.	Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.
A	243	0.18	1.27	E	1062	0.30	6.74
B	249	0.20	1.43	F	1023	0.20	5.64
Aver.....	246	0.19	1.35	Aver....	1043	0.25	6.19

Ratio of foot-pounds of unnotched to notched, 4.68. Ratio of maximum load of unnotched to notched, 4.24.

TABLE 11.—*Slow-bending Results on 8 Per Cent. Cu-Al Alloy (Lot 1990)*

Notched Bar				Unnotched Bar			
Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.	Specimen No.	Maximum Load, Lb.	Maximum Deflection, In.	Ft.-lb.
E	239	0.09	0.43	I	1130	0.07	2.29
F	272	0.09	0.47	J	1016	0.08	1.81
G	264	0.09	0.55	K	1133	0.08	2.43
H	226	0.09	0.46	P	1000	0.08	2.17
Aver.....	250	0.09	0.48	Aver....	1069	0.08	2.18

Ratio of foot-pounds of unnotched to notched, 4.54. Ratio of maximum load of unnotched to notched, 4.28.

Typical slow-bending curves are given in Figs. 7, 8 and 9. Fig. 7 shows the effect of time in taking the readings in the slow-bending test.

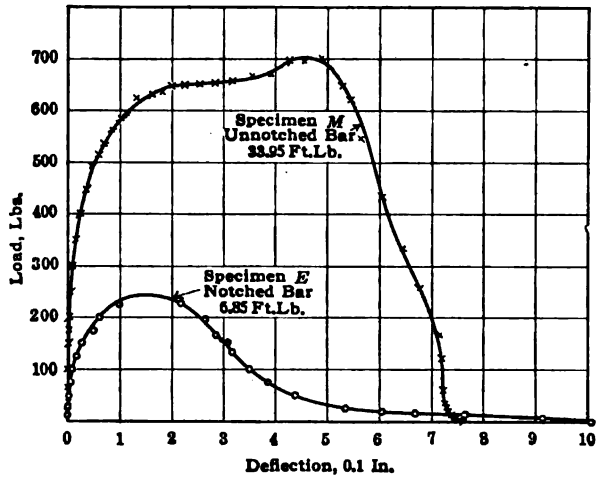


FIG. 8.—SLOW-BENDING CURVES OF PURE ALUMINUM (LOT 1987).

The lower curve represents the load that the specimen was able to hold 10 min. after the deformation had been applied; the higher curve gives

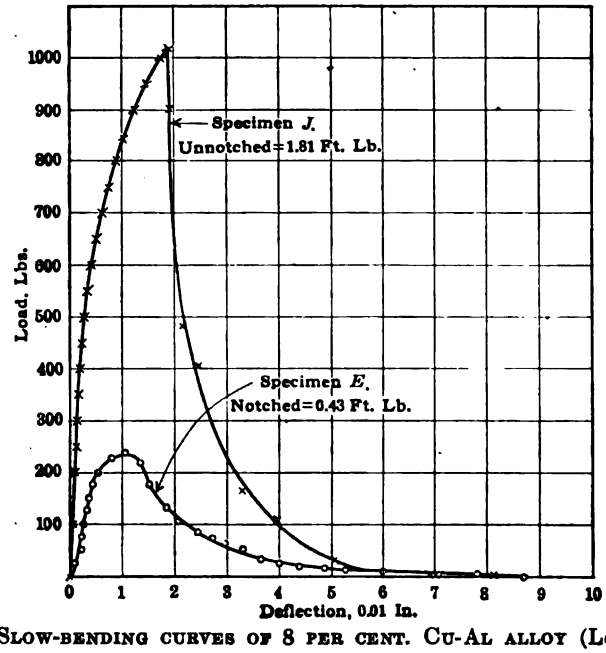


FIG. 9.—SLOW-BENDING CURVES OF 8 PER CENT. CU-AL ALLOY (LOT 1990).

the load that the specimen held when the deformation was first applied. The average rate of loading in this test was much lower than in the other

tests because, in the usual run of testing, it required only 3 to 5 min. to get the beam to stay balanced. The effect of this low average rate of loading on the maximum load is very evident from a study of Table 7. In other words, the slower rate of loading gives a lower maximum load and requires less foot-pounds to rupture the piece. This effect of time was also noticeable with the 2 per cent. copper alloy; but with the 4, 8 and 12 per cent. copper alloys, very little difference could be discovered in different rates of loading. Figs. 8 and 9 show the characteristic shapes of the notched and unnotched curves for pure aluminum and for 8 per

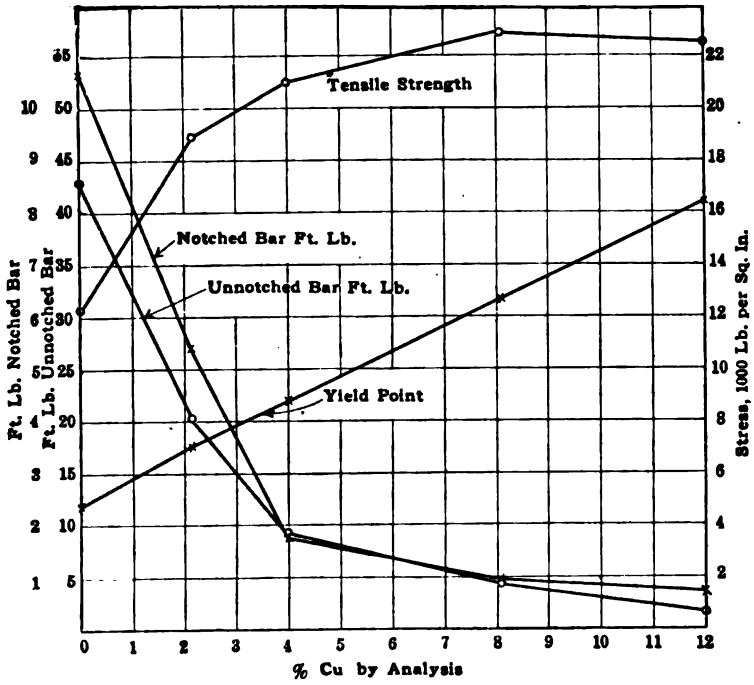


FIG. 10.—COMPARISON OF CHARPY IMPACT WITH YIELD POINT AND TENSILE STRENGTH.

cent. copper. The contrast between the pure aluminum and the 8 per cent. copper is very noticeable. The unnotched bar of the pure aluminum seems to hold on for a much greater deformation than does the notched bar. For the 8 per cent. copper alloy, the unnotched bar gives away much more suddenly than the notched bar.

Fig. 10 compares the Charpy impact results with the tensile strength and yield point. In general, as the tensile strength increases the impact resistance decreases. The increase in yield-point strength is nearly constant and seems to bear no direct relation to the shape of the Charpy impact curves.

Fig. 11 shows the elongation and the "product of tensile strength times elongation" as compared to the impact resistance. It has been

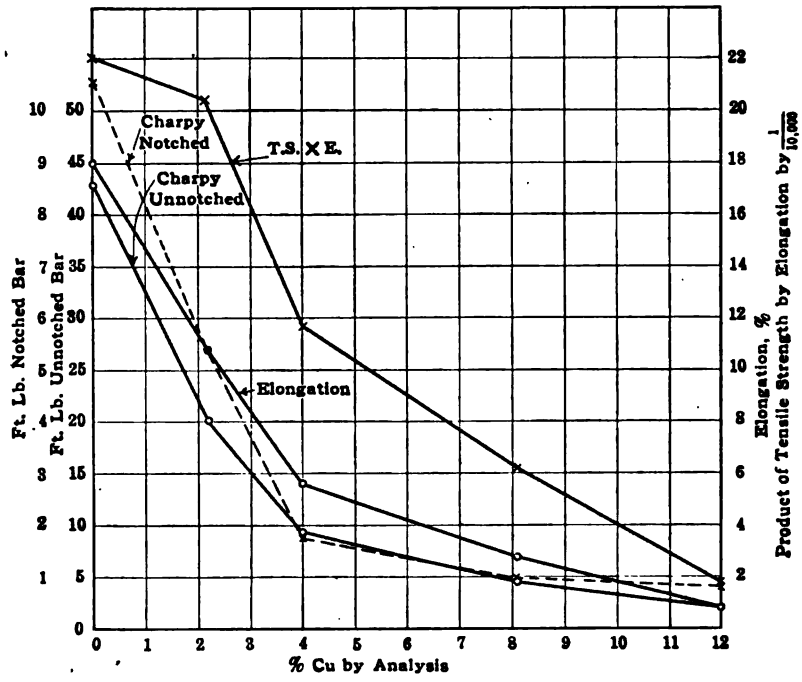


FIG. 11.—COMPARISON OF CHARPY IMPACT WITH ELONGATION AND PRODUCT OF TENSILE STRENGTH BY ELONGATION.

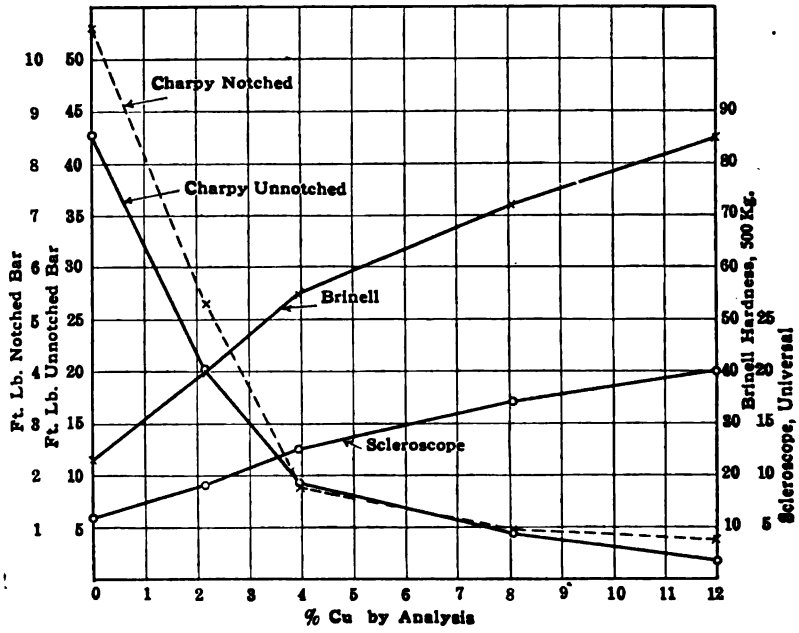


FIG. 12.—COMPARISON OF CHARPY IMPACT WITH BRINELL AND SCLEROSCOPE HARDNESS.

frequently stated that the impact resistance varies as the product of tensile strength times elongation. The general trend of this curve is similar to the curve of impact resistance, but the elongation curve follows the curve of impact resistance much more closely.

Fig. 12 shows the relation of Charpy impact resistance to Brinell and scleroscope hardness. In general, as the hardness increases the impact resistance decreases, but there is no direct similarity between the curves.

Fig. 13 gives a comparison of the slow-bending results with the Charpy results for both notched and unnotched specimens. The trend of all of these curves is approximately the same.

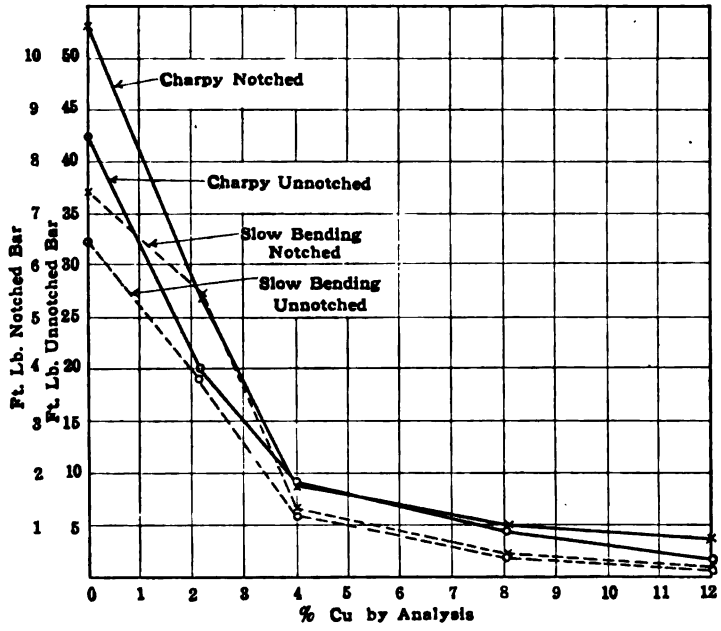


FIG. 13.—COMPARISON OF CHARPY IMPACT WITH SLOW-BENDING RESULTS.

Fig. 14 shows the relation between the foot-pounds energy absorbed in the slow-bending test with the maximum load for both notched and unnotched specimens. There does not seem to be any direct relation between the foot-pounds and the maximum load.

CONCLUSIONS

1. The Charpy impact resistance of copper-aluminum alloys decreases with increase in copper content, within the limit of these experiments (12 per cent. copper).

2. No direct relation has been discovered between the Charpy impact resistance and the more common physical properties. However, in

general, for this series of alloys the impact resistance decreases as the yield point, tensile strength, and hardness increase and the impact value follows more nearly the elongation than the "product of tensile strength by elongation," as is often stated.

3. The notch effect is very much less pronounced in this series of alloys than in steel. The ratio of unnotched to the notched resistance in the Charpy test varies from 2.4 to 4.8, the notched bar having one-half the breaking area of the unnotched. For steel bars having equal breaking areas, the writer has found the unnotched bar to offer four to five times as much resistance as the notched bar. The notched specimen

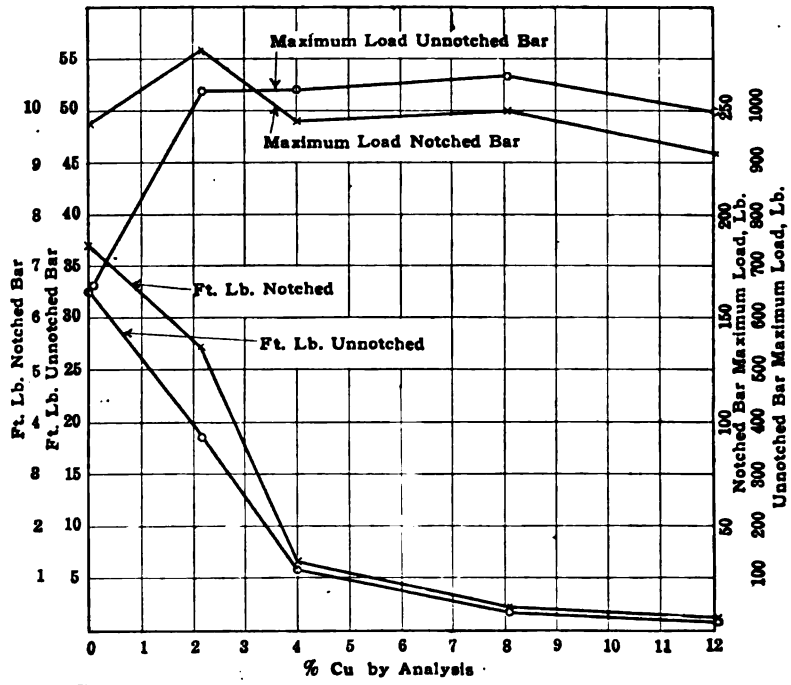


FIG. 14.—COMPARISON OF FOOT-POUNDS OF ENERGY WITH MAXIMUM LOAD IN SLOW-BENDING TEST.

was the same as used in these experiments, but the unnotched was of the shape that would be obtained by planing a notched bar to the root of the notch.

4. The slow-bending tests give the same order of results as the Charpy impact, but the ratio of energy absorbed in the slow-bending test to that of the Charpy test varies from 0.27 to 1.02. Captain Philpot[1] of England has reported that for steel this ratio is so nearly constant that he was led to the following conclusion: "The notched bar test made

[1] H. P. Philpot: Some Experiments on Notched Bars. *Proc.* Inst. Automobile Engineers (1918) **12**, 235.

in a pendulum testing machine is not essentially an impact test." The experiments reported on in this paper do not justify such a conclusion for these copper-aluminum alloys.

5. The ratio of maximum load of the unnotched bar to maximum load of the notched bar in the slow-bending test is very interesting. Since the strength of a beam varies as the square of its depth, the maximum load of the unnotched bar should be four times that of the notched bar if the notched bar were not further weakened by the "notch effect." This ratio varies from 2.73 for pure aluminum to 4.44 for the 12 per cent. alloy. This shows that the notch not only does not weaken pure aluminum but rather enables it to stand a proportionally higher load. For the 12 per cent. copper alloy, the weakening effect is small.

6. These results indicate that the Charpy impact test is a satisfactory test for aluminum alloys. When making this statement, the author fully realizes the danger of judging a material by its Charpy impact value without full consideration of the other physical properties. For instance, we must learn the proper Charpy figure combined with a given tensile strength and elongation that will give the most satisfactory shock-resisting aluminum alloy, just as the steel crankshaft manufacturer now knows the proper combination of Charpy impact value and yield-point strength that will give the most satisfactory service.

DISCUSSION

E. H. Dix, Jr.—As the notch is cylindrical, it would be hard to make, except perhaps with a form cutter. As this leaves tool marks, which have a tiny notch effect, it is rather hard to get consistent results with a milled notch. We have found that the drilled notch gives more uniform results. In steel specimens, grinding the notch gives about the same result as drilling.

Paul D. Merica,* Bayonne, N. J.—There is no question but that one of the disadvantages of our No. 12 alloy, which is used in this country for 97 per cent. of the castings, is its brittleness, or lack of resistance to shock, compared to an alloy having a lower copper content and consequent elongation. The author has presented data that make possible a comparison between the low-copper alloys and the No. 12. Is the impact test on such an alloy as No. 12 more sensitive to slight variations in composition than the elongation? One No. 12 alloy has an elongation of ½ to 1½ per cent. Within these limits does the impact test give a greater indication of impact energy absorbed? Could one derive a fairly good impression of the impact resistance of material from the consideration of elongation?

* International Nickel Co.

In the low-copper alloys, the fracture is not so likely to be intercrystalline, because of the non-continuity of the eutectic, as it is in the case of the higher copper alloys. Is there a greater difference in the relation between the impact resistance and the tensile strength in the low-copper alloys, or perhaps in wrought alloys, than in the higher copper ones?

E. H. DIX, JR.—We tested a number of alloys of different composition, where the physical properties vary so slightly that it is impossible to note any difference in the elongation though there is considerable difference in the impact figure.

We have not examined fractures metallographically. Of course, the fracture of a low-copper alloy is very different from that of the high-copper, and it is easier to study the fracture from an impact test than from a tensile test, for more of the actual grain formation is seen.

F. G. ALLIS.—Do you think that the shape of the original casting affects the results? Does the pouring temperature affect the impact strength? Are any of the national societies trying to standardize the impact test, size of bar, and so forth?

E. H. DIX, JR.—During the war I was in a laboratory that functioned as an arbitrator. Our first problem was the impact test. Some of our inspectors worked in plants using the Charpy machines: some in plants using the Izod, and some had the Olsen machine, but no available data gave the relations of the different machines. Besides, different notches were used. We did considerable work, the results of which were published by the American Society for Testing Materials.

In these experiments the object was to eliminate all possible variables, except the impact test, so the pouring temperature was kept constant. The bars were cast long enough to get four specimens out of each one, partly because it was desirable to get as many molds as possible and partly to permit the comparison of the variation in specimens taken from the same bar with those taken from another bar in the same mold; these variations were not at all pronounced.

New Process for Making Fifteen Per Cent. Phosphor-Copper

By P. E. Demmler,* East Pittsburgh, Pa.

(Columbus Meeting, October, 1920)

Phosphorus combines with copper in various proportions, forming true alloys, some of which are of commercial importance. These materials find wide application as deoxidizers and as a means of introducing phosphorus into other alloys, as in phosphor-bronze.

Phosphor-coppers containing 10 and 15 per cent. of phosphorus are the commercial grades that are most generally offered. Each has certain advantages when used in making other alloys. The 10 per cent. grade of phosphor-copper has an advantage over the 15 per cent. in that it has a much lower melting point and can be prepared by certain methods with a much lower loss in phosphorus. The 15 per cent. grade has the advantage of lower freight rates per unit of phosphorus and, by the method to be described, a uniform product can be prepared with practically no loss of phosphorus. Alloys of copper and phosphorus containing any desired percentage of phosphorus lower than 15 per cent. can be prepared by melting together the requisite amounts of copper and 15 per cent. phosphor-copper.

Processes for making phosphor-copper may be divided into two classes as follows: (1) Those depending on the smelting of phosphate rock or superphosphate of calcium with copper or copper-bearing materials, and coal or other carbonaceous material; (2) those depending on the direct combination of metallic copper and elemental phosphorus.

A number of formulas for preparing phosphor-copper according to the first method have been published. *The Metal Industry*[1] gives the following: Superphosphate of calcium, 60 lb.; granulated copper, 30 lb.; finely powdered coal, 10 lb. Similar formulas are given by Brannt[2] and others, and detail variations are covered by patents, such as those of L. A. Jeffs[3] and H. A. Webster.[4]

Among the objections to this method of producing phosphor-copper are the large amounts of raw material and resulting slag to be handled, and the difficulty of getting a satisfactory fusion. S. Skowronski[5] found that at 1300° C. (2372° F.) it was impossible to get a good fusion

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* Chemical and Experimental Laboratory, Westinghouse Elec. & Mfg. Co.

[1] N. Y. (Aug., 1917) 351. [2] "Metallic Alloys," 245. [3] U. S. Patent 1268849.
[4] U. S. Patent 1265150. [5] Private communication.

even when silica sand was added as a flux. Globules of 15 per cent. phosphor-copper were obtained in the experiment.

Methods of the second class, depending on the direct combination of copper and phosphorus, are generally used for the preparation of phosphor-copper. The usual practice seems to be to add the phosphorus to the molten copper by means of phosphorizers. The best practice by this method entails a phosphorus loss of at least 25 per cent. Besides the phosphorus loss, there is also the objection of the great danger of burns to the workmen handling phosphorus around the phosphorizers and molten metal.

The danger attending the handling of phosphorus may well be emphasized. Ordinary yellow phosphorus, such as is generally used, melts at 44.2° C. (111.5° F.). It will take fire at 34° C. (93° F.); that is, the heat of the hand is sufficient to ignite a piece of dry phosphorus. Material of this nature must be handled with exceeding care. The danger and wastefulness of methods by which phosphorus is added directly to molten copper have been referred to previously in technical literature.[6]

Various methods have been suggested for obviating the objections referred to. E. G. Burr[7] places the phosphorus in a retort adjustably mounted above the crucible containing the molten metal; the vapor from the material in the retort passes into the molten metal through a pipe dipping into the metal. E. Schulte[8] forces the molten phosphorus, air being excluded, into molten copper by hydraulic pressure. Both these methods aim to avoid the handling of phosphorus near the molten copper, but serious difficulties are met in the carrying out of either of these processes.

Experiments of the author have shown that a uniform 15-per-cent. phosphor-copper could be produced by passing phosphorus vapor over heated copper. The most satisfactory temperature of the copper was found to be 400° C. (752° F.) Phosphorus boils at a comparatively low temperature, approximately 290° C. (554° F.), and when this vapor passes over heated copper, combination takes place immediately with incandescence and incipient fusion. Pieces of copper wire up to ¼ in. in diameter are completely phosphorized by this method. The advantages of a process of this kind can readily be seen.

An apparatus having a capacity of about 130 lb. of phosphor-copper was constructed to demonstrate the commercial value of this method; its main features are shown in the accompanying illustration. This apparatus consists of a retort for heating and distilling the phosphorus, a container for the copper, and fittings to connect the two. Suitable supports are also provided. The apparatus is made entirely of iron,

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[6] J. L. Jones: *The Metal Industry* (Aug., 1917) 351.

[7] Brit. Pat. 125785, May, 1918. [8] German Pat. 281293, Mar., 1913.

which is not attacked by phosphorus at the temperature of the operation. Means are provided for heating the phosphorus and copper separately.

To operate, phosphorus is placed in the retort, clean copper scrap (such as wire, turnings or millings) is placed in the copper container, and the two are connected. Tight joints should be made by using suitable gaskets to prevent loss of phosphorus. A hole drilled into the plate covering the end of the copper container prevents increase of pressure within the apparatus. The copper is heated to 400° C. before heat is applied to the phosphorus. With the small apparatus we have been able to distill the phosphorus at the rate of 30 lb. per hour.

Phosphorization to 15 per cent. phosphor-copper takes place in one step, no intermediate products being formed if conditions as to temperature are observed. When more copper is charged than is necessary to

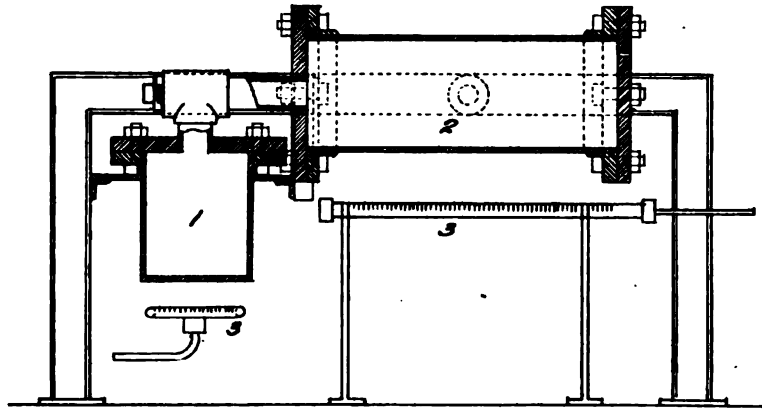

FIG. 1.

combine with the phosphorus used, the copper nearest the phosphorus retort will be completely phosphorized, while that farther away is unchanged and can readily be separated from the phosphorized product. The same action was observed when phosphorus vapor was passed over heated copper turnings in a glass tube several feet long. The progress of phosphorization could be observed and, whenever the supply of phosphorus ceased, there was a sharp separation of the 15 per cent. phosphor-copper and the unphosphorized copper.

The product of phosphorization by this method is a black, brittle mass. Freshly fractured surfaces show a bright luster. It is interesting to note that phosphorized wire frequently is hollow, presenting the appearance of tubes. Owing to the incipient fusion due to the heat of the reaction, the phosphor-copper may be removed from the apparatus in lumps and used in this form, or it may be remelted and cast in any desired mold.

The products from several heats made as described were melted in crucibles and cast into ingots. A composite sample made by taking pieces from each ingot, pulverizing and mixing, analyzed 15.11 per cent. phosphorus. Pieces taken at random from the several heats showed a very uniform phosphorus content of 14.9 per cent. to 15.1 per cent. Red phosphorus was used in several cases and the same product obtained, but owing to the much slower rate of volatilization of the red phosphorus, the rate of phosphorization is correspondingly less than when the ordinary yellow phosphorus is used.

The method of making phosphor-copper containing 15 per cent. of phosphorus, as outlined above, has the following marked advantages over other methods:

(1) The copper need not be heated over 400° C. (2) The phosphorus need not be handled near hot or molten metal. (3) There is no loss of phosphorus. (4) The product is uniformly 15 per cent. phosphor-copper.

Neither the 10 per cent. nor the 15 per cent. phosphor-copper represent definite, simple chemical compounds. Heyn and Bauer[9] state that the phosphorus exists in the alloys as Cu_3P and Cu_5P_2, which compounds contain 14.00 and 16.34 per cent. phosphorus, respectively, from which it would appear that the 15 per cent. phosphor-copper may be a mixture of the above-mentioned phosphides in almost equal proportions. The uniformity of the product obtained in all the different heats made by this method would indicate that the reaction between phosphorus and copper reaches its equilibrium at a definite point each time under the conditions as outlined above.

The same principle of forming compounds or alloys of volatile with less volatile elements may be used for preparing other alloys than phosphor-copper. We have prepared in the laboratory, by the method described, compounds of phosphorus with tin, zinc, and cadmium; of arsenic with copper, silver, lead, and cadmium; and of selenium with copper.

DISCUSSION

P. E. Demmler.—The report of 15 per cent. was obtained by taking all the heats made in the two styles of apparatus, the one of 30 lb. and the other of 130 lb. capacity; melting them together in large crucibles, casting them, and then sampling and analyzing them. The 15.1 per cent. represents the analysis of the remelted sample.

As near as it is possible to tell from the appearance of the surface there is little loss of phosphorus in remelting. If charcoal is placed on material in the crucible, a phosphorus flame is almost entirely absent. We have not had the 15 phosphor-coppers catch fire after they are cast.

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[9] *Jnl.* Soc. Chem. Ind. (1906) **25**, 1047.

A small ingot cast three years ago has at present a slight green scum, which we attribute to the presence of a small amount of slag, because the inside of the ingot is apparently sound.

W. K. FRANK, Pittsburgh, Pa.—Is it not possible that the scum is the excess phosphorus that is held in solution by the Cu_3P?

P. E. DEMMLER.—It would probably take a metallographic examination to determine anything of that kind. I would not care to say offhand.

G. H. CLAMER, Philadelphia, Pa.—What has been your experience with phosphor tin made by this process?

P. E. DEMMLER.—The phosphor-tin made by this process contained about 13 per cent. of phosphorus and could not be remelted without decomposition but it readily dissolved in molten tin. When the tin-phosphorus alloy contained as high as 5 or 6 per cent. phosphorus, it could not be melted without decomposition. It was only when the alloy contained less than about 3 per cent. of phosphorus, preferably about 2 per cent., that there was stability in melting. Above 2 per cent. or 3 per cent. there was always a burning of phosphorus on attempting to melt, showing a rapid decomposition of the phosphor-tin.

Transition Phenomena in Amalgams

By Arthur W. Gray,* Ph. D., Milford, Del.

(Columbus Meeting, October, 1920)

The thermal analysis of a metal or an alloy is ordinarily made with the aid of heating and cooling curves in which transitions are indicated by the rapid changes in curvature that accompany changes in the rate of heat absorption or evolution. Analysis by the method that depends on the change in thermal expansivity is not customary, partly, at least, because of the difficulties involved in making the necessary measurements. However, under certain circumstances, the dilatometric method of analysis may possess advantages over the thermometric method that will justify the additional trouble required.

The addition of 1 per cent. of zinc to an alloy has been found to produce upon the volume changes that take place during transition effects that suggest the possibility of using the dilatometric method of thermal analysis as a rather sensitive means of obtaining chemical information. Although the illustrations presented in this paper are drawn from data obtained during an investigation of dental amalgams, similar phenomena can doubtless be observed with other alloys.

Some of the results found during an investigation made in 1917[1] have been confirmed by data on the thermal expansivity of amalgams published by Souder and Peters of the Bureau of Standards in reporting tests of dental materials.[2] Although the Bureau of Standards made experiments for the purpose of discovering effects of including zinc as one of the constituents of a dental alloy—a matter much discussed in dental literature but without the presentation of reliable experimental evidence to support the views of either side—the reports of the tests made by the Bureau give the impression that certain striking phenomena associated with the presence of zinc were not noticed. Among such phenomena are those connected with the conditions that determine whether or not a specimen of amalgam becomes covered with droplets from which crystals develop.

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* Director of Physical Research, The L. D. Caulk Co.

[1] A. W. Gray: Metallographic Phenomena Observed in Amalgams. *Trans.* (1919) **60**, 657–697. *Jnl.* National Dental Assn. (1919) **6**, 513–531 and 909–925.

[2] W. H. Souder and C. G. Peters: An Investigation of the Physical Properties of Dental Materials. *Dental Cosmos* (1920) **62**, 305–335. Bureau of Standards *Tech. Paper* 157 (1920) 1–40.

Crystal Growth During Transition

During the earlier investigation and also during various crushing strength tests, the author had noticed that amalgams from alloys containing 1 per cent. or so of zinc became studded with brilliant crystals when heated into the transition region, while similarly treated amalgams from non-zinc alloys did not.

These crystals are beautiful six-sided tablets, which apparently belong to either the hexagonal or the orthorhombic system, and project from the surfaces of the amalgam test cylinders.

All the test cylinders upon which observations have been made were prepared in the manner described in the previous paper,[3] and the conditions likely to influence results were definitely known and controlled. In particular, each specimen was molded under a measured packing pressure applied to the piston that condensed the amalgam into a test cylinder. The amalgams were made from alloys having approximately the compositions given in Table 1. These alloys will hereafter be referred to by the letters at the heads of the columns in the table.

Table 1.—*Compositions of Amalgam Alloys**

	A	B	C	D	E	F	G	H
Silver	75	69	68	68	68	70	70	54
Tin	20	26	27	26	26	27	27	30
Copper	5	5	5	5	5	3	3	16
Zinc	0	0	0	0	1	0	1	0
Total	100	100	100	99	100	100	101	100

*The composition of each alloy is here stated in terms of parts by mass. That of alloy D is expressed in such a way as to point out that D is made by omitting the 1 per cent. of zinc from alloy E. Similarly G is made by adding 1 per cent. of zinc to an alloy having the composition F.

Since the specimens were concealed within an oil bath or within an electric furnace while the thermal analysis measurements were in progress, some specimens were also placed in glass test tubes and immersed, with a mercurial thermometer, in a beaker of water that was slowly heated by a Bunsen burner. It was then found that whenever amalgams containing zinc were heated into the transition region, minute drops resembling mercury oozed through the surface at numerous points and gradually increased in size. As a rule, the drops were not noticed until the water surrounding the test tubes reached a temperature of about 80° C.

When amalgam cylinders from alloy E that were some months old, and therefore thoroughly hardened, were warmed until the droplets appeared,

[3] A. W. Gray: *loc. cit.*

and then were cooled gradually, crystals suddenly developed when the temperature of the water-bath reached about 62° C. The crystallization tem-

FIG. 1a. FIG. 1b. FIG. 2.

FIG. 1.—CRYSTALS DEVELOPED DURING TRANSITION OF DENTAL AMALGAM CONTAINING ZINC. MAGNIFICATIONS 2 AND 20 DIAMETERS.

FIG. 2.—AMALGAM FROM ZINC ALLOY E; PACKED UNDER 100 KG. PER CIRC. CM. AND HEATED SOME MONTHS LATER. MAGNIFICATION 4 DIAMETERS.

FIG. 3. FIG. 4.

FIG. 3.—AMALGAM FROM ZINC ALLOY E; PACKED UNDER 800 KG. PER CIRC. CM. AND HEATED SOME MONTHS LATER. MAGNIFICATION 4 DIAMETERS.

FIG. 4.—AMALGAM FROM ZINC ALLOY E; PACKED UNDER 100 KG. PER CIRC. CM. AND HEATED 2 HR. LATER. MAGNIFICATION 4 DIAMETERS.

perature seems to be rather sharply defined, and to be, at least approximately, the same for amalgams molded under 100 kg. per circ. cm. as for

amalgams molded under 800 kg.[4] The packing pressure, however, exerted a marked effect on the size and the distribution of the droplets and crystals. As the pressure increased, the droplets and crystals became smaller and more numerous, as shown by Figs. 2 and 3. By heating for a

FIG. 5.—AMALGAM FROM NON-ZINC ALLOY D; PACKED UNDER 25 KG. PER CIRC. CM. AND HEATED 1 YEAR LATER. MAGNIFICATION 4 DIAMETERS.

sufficient time cylinders that had been packed under 100 kg. per circ. cm., so much mercury could be driven out that some would remain in the liquid state after the crystals had formed and the amalgam cooled to room temperature.

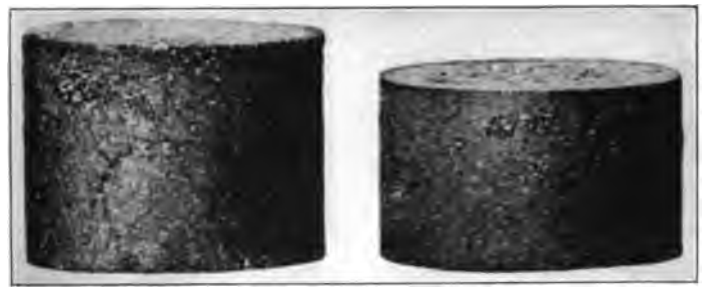

FIG. 6. FIG. 7.

FIG. 6.—AMALGAM FROM NON-ZINC ALLOY D; PACKED UNDER 25 KG. PER CIRC. CM. AND HEATED $1\frac{1}{2}$ HR. LATER. MAGNIFICATION 4 DIAMETERS.

FIG. 7.—AMALGAM FROM NON-ZINC ALLOY D; PACKED UNDER 400 KG. PER CIRC. CM. AND HEATED 3 HR. LATER. MAGNIFICATION 4 DIAMETERS.

In the case of amalgams that were only a few hours old, fewer drops were exuded, but they were considerably larger. Upon cooling, the crystals seemed to form more gradually and in somewhat rounded groups. In

[4] As in the author's previous paper on amalgams, all pressures are for convenience expressed in terms of kilograms-weight per circular centimeter. This is analogous to the current practice of using the circular mil as a unit for expressing cross-section areas of wires. The use of the circular centimeter instead of the square centimeter avoided much unnecessary computation in expressing the results of about five thousand tests on cylindrical specimens 1 cm. in diameter.

1 kg. per circ. cm. $= \frac{4}{\pi}$ kg. per sq. cm. = 18.10 lb. per sq. in.

general, the faces and angles were not so sharply defined. The blurring of the crystal boundaries, possibly because of excess mercury, was particularly noticeable when the packing pressure was fairly low. Fig. 4 shows a cylinder from alloy E packed under 100 kg. per circ. cm. and heated when about 2 hr. old.

Non-zinc amalgam cylinders old enough to have become thoroughly hardened yielded no drops or crystals upon heating, except in two cylinders a year old made from alloy D that had been packed under a pressure of 25 kg. per circ. cm. The high mercury content that ordinarily accompanies such a low packing pressure was increased by the addition of surplus mercury expressed during the condensation of the amalgam. This surplus coated the surfaces of the cylinders when they were removed from the mold, and diffused inwardly as the amalgam hardened. The crystals that formed on these cylinders (Fig. 5) were smaller and fewer than those observed on zinc amalgams under similar conditions.

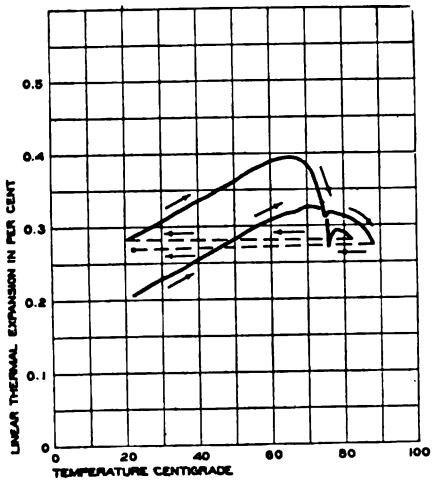

FIG. 8.—THERMAL EXPANSION OF AMALGAM FROM NON-ZINC ALLOY F.

Freshly prepared amalgams from non-zinc alloys exuded droplets; these, however, unlike the droplets exuded by the amalgams from zinc alloys, did not, as a rule, develop crystals. Usually, these droplets became reabsorbed as the heating continued, or as the amalgam cooled. Whenever crystals did form after heating freshly prepared non-zinc amalgams, they were very few and very small. Figs. 6 and 7 show crystals on cylinders from alloy D a few hours old; the first was packed under 25 kg., the other under 400 kg. per circular centimeter.

THERMAL EXPANSION

Thermal-expansion measurements were made by means of the lever dilatometer used for reaction-expansion measurements.[5] The cylindrical specimen of amalgam was directly immersed in a slowly heated bath of stirred oil. Observations of temperature and of change in diameter of the specimen were taken once a minute.

The dilatometer indicated not the total expansion of the specimen, but the difference between this and four-fifths the expansion of a similar cylinder of invar, which formed part of the instrument. Since a knowl-

[5] A. W. Gray: *loc. cit.*, 681.

edge of the exact expansivity of this invar cylinder was unnecessary, it was not determined. Therefore, the thermal expansivity values given later must be increased by adding to each the same correction, approximately one millionth. In determinations of reaction expansion, this correction vanishes, because the measurements of a given specimen's diameter changes are all made at the same temperature.

The amalgams from the non-zinc alloys tested yielded expansion-temperature curves similar to those in Fig. 8, which represents an amalgam made from alloy F. The curves show results of heating the same specimen on successive days; the arrows indicate the direction of the temperature change. The observations were so close together that it was impossible to distinguish individual measurements. Dash lines connect

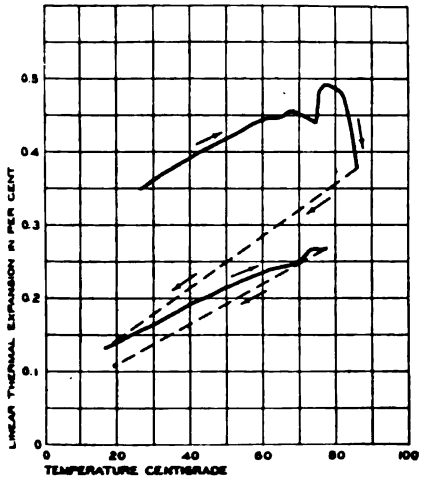

FIG. 9.—THERMAL EXPANSION OF AMALGAM FROM NON-ZINC ALLOY C.

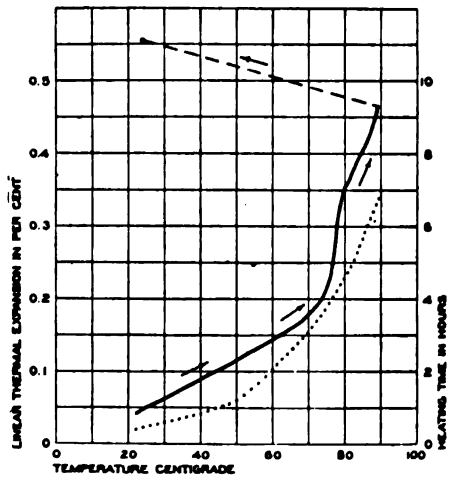

FIG. 10.—THERMAL EXPANSION OF AMALGAM FROM ZINC ALLOY G.

points corresponding to the last observation of one day and the first observation of the following day.

The typical curve for a non-zinc amalgam is characterized by an almost straight portion that slopes upwards until the transition begins, when a rapid drop to a sharp minimum occurs. This is followed by a slight but rapid rise, which is succeeded by a further drop. Reheating an amalgam yielded a curve of the same general shape as that obtained during the first heating, but with the transition region characteristics less pronounced.

In the case of certain non-zinc amalgams, especially those from alloys low in silver and high in copper (like alloy H) these characteristics, though noticeable, were not very prominent. This observation is confirmed by the expansion curves for K and L given by Souder and Peters.[6]

[6] *Loc. cit.*, Fig. 8.

Fig. 9 represents an amalgam from an alloy having the composition of C. It is the same as alloy A of Souder and Peters. As far as it goes, their curve for this agrees with that here shown, but they began cooling before reaching the maximum. Moreover, they give no data as to the behavior of an amalgam the second time it is heated into the transition region. That the contraction accompanying transition may reduce the diameter of an amalgam cylinder below the diameter it previously had at room temperature is shown by Fig. 9 and by the corresponding curve of Souder and Peters.

Amalgams from zinc alloys usually yield expansion curves similar to those shown by Souder and Peters for their alloys H and B. Typical curves of this kind are also shown by Figs. 10, 11, and 12. The outstanding characteristic of such a curve is a gradually increasing upward

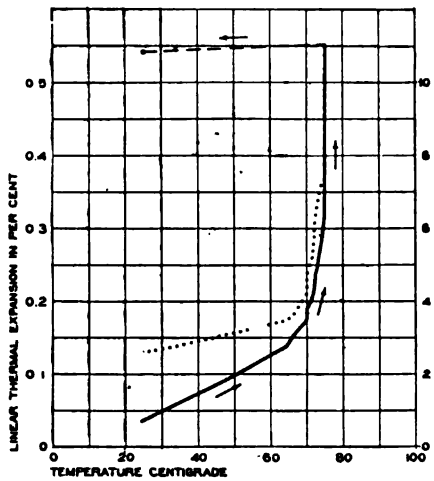

FIG. 11.—THERMAL EXPANSION OF AMALGAM FROM ZINC ALLOY E, SHOWING CONTINUED GROWTH AT CONSTANT TEMPERATURE DURING TRANSITION.

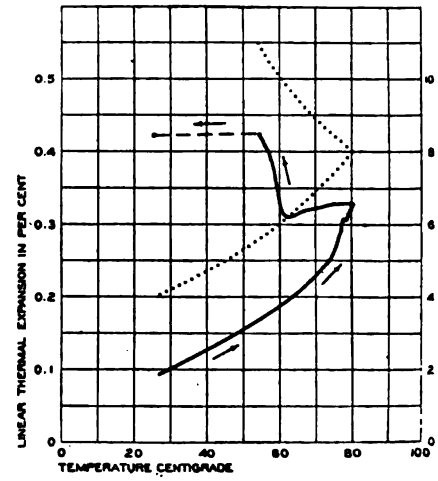

FIG. 12.—THERMAL EXPANSION OF AMALGAM FROM ZINC ALLOY E, SHOWING CONTINUED GROWTH EVEN DURING FALLING TEMPERATURE.

curvature, which rapidly changes into a steep rise as the transformation gets under way. Once this rapid expansion is well started, it will continue for some hours, although the temperature be held constant, or even lowered. The great influence that a little zinc exerts upon the transition is strikingly brought out by a comparison of Figs. 8 and 10. The test specimens for both F and G were prepared under conditions as nearly identical as possible. They were made by triturating 3 gm. alloy with 6 gm. mercury for 6 min. and then molding under a pressure of 141 kg. per circ. cm. applied 8 min. The dotted curves in Figs. 10, 11, and 12 indicate the rates of temperature change. The change of heating rate near 50° C., Fig. 10, produced no noticeable effect on the initial straight portion of the expansion curve.

Figs. 11 and 12 show how the transition continues after it is once well started, even though the temperature be held constant or even lowered. Both of these figures represent observations on alloy E. The test specimens were prepared as for Figs. 8 and 10, except that the amalgam represented by Fig. 11 was packed under 400 instead of under 141 kg. per circ. cm. In Fig. 11, the heating rate was not reduced until just after the beginning of transition became apparent. Growth continued while the temperature was held constant at 70.0° C. for 30 min. Later, a continued expansion was observed for 2¼ hr. while the specimen was maintained at 75° C.

In the case of Fig. 12, after the temperature had reached 80° C., heating was discontinued and the bath allowed to cool. At first the ordinary thermal contraction predominated; but as the transition got well under way, the expansion completely overshadowed this contraction, even though the temperature had fallen considerably below that at which rapid growth began during warming. The gradually increasing upward curvature noticeable in amalgams containing zinc is very prominent in this curve, perhaps because of the high mercury content that accompanies the rather low packing pressure.

A curve similar to the first two portions of that in Fig. 12 is shown by Souder and Peters for their alloy B. Their curve, however, lacks the rapid expansion that the author observed as the cooling was continued below 60° C.

TABLE 2.—*Linear Expansivity of Amalgams near* 37.5° C.

Specimen	Alloy	Mercury-Alloy Ratio	Trituration Time Minutes	Packing Pressure (Kilograms per Circular Centimeter)	Expansivity (Millionths per degree C.)
I*a*	E	2.00	6	141	25.8
II*a*	E	2.00	6	400	24.2
III*a*	E	2.00	6	1131	24.2
III*b*	E	2.00	6	1131	25.0
IV*a*	E	1.60	4	400	23.8
IV*b*	E	1.60	4	400	24.2
V*a*	G	2.00	6	141	26.7
VI*a*	F	2.00	6	141	26.8
VI*b*	F	2.00	6	141	27.5
VII*a*	C	1.60	4	400	28.3
VII*b*	C	1.60	4	400	25.0
VIII*a*	H	1.60	4	400	23.3
VIII*b*	H	1.60	4	400	25.8

That zinc exerts little influence on the expansivity until the transition region is approached is evident. That it is not the only factor determin-

ing the behavior during transition is indicated by Souder and Peters' curve for alloy P, which begins transition with a contraction, although it contains 5 per cent. of zinc. The fact that this particular alloy contains only 60 per cent. of silver may have some bearing.

Table 2 presents values found for the linear thermal expansivity of several amalgams near body temperature (37.5° C.). The letter following the specimen number indicates whether the measurements were made during the first or the second heating into the transition region. The horizontal line separates the data on the zinc alloys E and G from the data on the non-zinc alloys F, C, and H. As the third and fourth columns of the table indicate, the amalgamation was thorough. In each case a liberal supply of mercury was triturated with the alloy; and the trituration time was excessive for the 3 gm. alloy used in making a cylinder. The packing pressure given in the fifth column was maintained 8 min. during the molding of the amalgam.

All the specimens had been used in reaction expansion tests some months before these thermal expansion measurements were made. During the interval, the specimen had been kept in an incubator at body temperature. In the last column is recorded, in millionths per degree centigrade, the difference between the thermal exp ansivity of each amalgam and four-fifths the expansivity of the invarcylinder. As already stated, a correction of approximately one millionth must be added to each value given in the table to obtain the expansivity of the amalgam itself. Omission of this correction in no way affects the determination of differences among the expansion coefficients of the various amalgams.

The amalgam from which specimen IV was made was subjected to a peculiar thermal treatment. Immediately after trituration, it was rapidly cooled by being laid upon CO_2 snow for 10 min. Then it was softened by slightly warming it in the hand; but before reaching room temperature it was molded into a test cylinder for determining reaction expansion.[7]

Table 2 shows no great differences in the expansion coefficients of amalgams prepared from alloys varying considerably in composition. The range in silver is from 54 to 70 per cent.; in tin, from 26 to 30; in copper, from 3 to 16; and in zinc, from 0 to 1. Warming into the transition region increased the body temperature expansivity by a few per cent., except in the case of alloy C. In this case there was a reduction in expansivity.

The results for alloy E indicate that variations in amalgamation and

[7] The amalgam was subjected to this treatment so as to test a process advocated for prolonging the time that a dentist might take while inserting a filling made from one of the high-grade, and, consequently, rapidly setting alloys. Lowering the temperature retards the reaction that causes the amalgam gradually to change from a soft, plastic mass to a hard substance of great strength.

in packing pressure are without much effect upon the thermal expansivity, although such variations profoundly modify reaction expansion, crushing strength, mercury content, and other properties, especially when the packing pressure is low. The expansivity of specimen I appears to be somewhat greater than that of the other specimens from alloy E. Perhaps this is attributable to the higher mercury content resulting from the lower packing pressure.[8] The average deviation of the coefficients found for the five other amalgams from the same alloy differs from the average of the five coefficients by only ± 0.3 in 24.3, or 1.2 per cent. The difference between the smallest and the largest of the five values is 1.2, which is 4.9 per cent. of the average.

Souder and Peters report the three values 25.0, 24.7, and 28.0 for the amalgams that they prepared from substantially the same alloy as E.[9] The average deviation of these coefficients from their average is ± 1.4 in 25.9, or 5.4 per cent.; the difference between the smallest and the largest is 3.3 or 12.7 per cent.

These comparatively large deviations are not ascribable to the type of expansion apparatus used by Souder and Peters, because their instrument (Priest's modification[10] of the Fizeau dilatometer) is capable of measuring small elongations with high accuracy. The deviations are due, rather, to their failure to control the packing pressure and, consequently, the mercury content of the amalgam specimens. Experiments on specimens packed by dental methods are useful for showing results to be expected in dental practice; they are not so useful when the object is to make precise comparisons of similar materials.

The similarly prepared amalgams from alloys F and G yielded almost identical expansivities at body temperature the first time they were heated; the one per cent. of zinc in the latter does not show any effect until transition begins.

Thermal Analyses by Modified Roberts-Austen Method

Thermal analyses of some amalgams were made by the Roberts-Austen differential method changed so that the primary thermometer gave the temperature of the neutral body instead of the temperature of the specimen under investigation. The apparatus shown in Fig. 13 was employed. The bulb of a mercurial thermometer serves as neutral body. Bound close against this by several layers of silk is one junction of a copper-con-

[8] Irregularities in results obtained at the Bureau of Standards with hand-packed amalgams appear to support this view.

[9] *Loc. cit.*, 316. Their alloy C.

[10] I. G. Priest: A New Interferential Dilatometer. Bureau of Standards *Sci. Paper* 365, *Bull.* 15 (1920) 669–678.

stantan thermoelement; the other junction is located near the thin, drawn-out tip of the glass tube that encloses both thermometer and thermoelement. This tip is inserted in a hole drilled axially into the specimen; therefore the thermoelement determines the temperature difference between the specimen and the thermometer bulb. It was connected directly in series with a Leeds & Northrup Type P galvanometer, and with sufficient resistance to yield critical damping. The sensitivity was such that one scale-division corresponded to 0.05° C., so that readings to 0.01° C. were easily obtained.

FIG. 13.—APPARATUS USED FOR THERMAL ANALYSIS BY MODIFIED ROBERTS - AUSTEN METHOD.

The specimen and the neutral body, surrounded by a glass tube and a few millimeters of asbestos, were simultaneously heated within a small electric furnace supplied with current from a portable storage battery. The resistor was wound around a piece of iron pipe. A thermoelement with one junction just under the heating coil and the other close to the inside wall of the pipe, indicated the radial temperature gradient. By gradually reducing the control resistance so as to keep this gradient constant while the temperature was being increased, a regular heating rate was easily maintained. This was close to 0.5° C. per minute. Both the mercurial thermometer and the thermoelement galvanometer were read every quarter minute.

A typical set of heating and cooling curves is reproduced in Fig. 14, which shows the behavior of amalgam from alloy B. The arrows to the left indicate the direction of the temperature change; the adjacent numbers indicate the consecutive heatings of the same specimen of amalgam. The temperatures at the bottom of the chart are those of the specimen. The distance between one horizontal line and the next represents a temperature difference of 2.5° C. between specimen and neutral. In the following three charts the same distance represents 1° C.

The thermal analysis curves of Fig. 14 exhibit the following prominent features: The first time the amalgam is warmed, the heat absorption marking transition takes place rather suddenly. It is also fairly intense, resulting in a temperature difference of about 5° C. between the specimen and the neutral body. Upon subsequent warmings, the absorption begins about 5° C. lower than upon the first warming; it also proceeds much more gradually and is completed

at a lower temperature. The magnitude of the absorption is considerably less during the second than during the first heating. It is still less during the third; but thereafter little or no change is observable. The sharp minima in the several heating curves occur at nearly the same temperature, which decreases slightly with each warming. The temperatures observed upon the five consecutive heatings of this specimen were 74.4°, 73.7°, 73.6°, 73.3°, and 73.1° C. The temperature region marked by rapid heat absorption agrees closely with the region marked by the first rapid contraction in the case of the non-zinc amalgams (Figs. 8 and 9), and by the rapid expansion in the case of the amal-

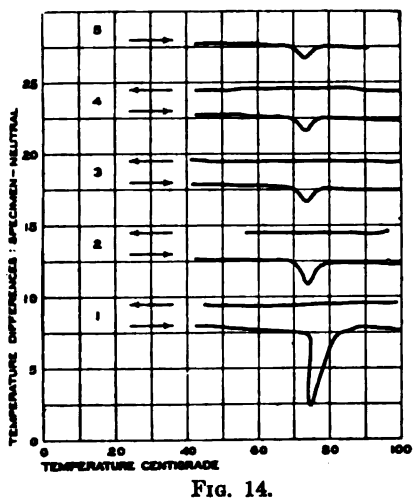

FIG. 14.

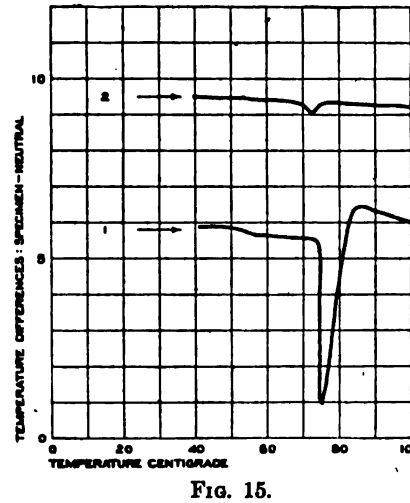

FIG. 15.

FIG. 14.—TYPICAL THERMAL ANALYSIS CURVES, SHOWING CHANGES ON CONSECUTIVE HEATINGS; AMALGAM FROM ALLOY B.
FIG. 15.—AMALGAM FROM ALLOY A.

gams containing zinc (Figs. 10, 11, and 12). During cooling throughout a temperature interval of 60° C., no corresponding evolution of heat is evident. Fig. 15 is a striking example of smaller heat absorption during the second warming through the transition region. The temperatures marked by the minima are 75.0° and 72.3° C.

Fig. 16 shows the effect of adding 1 per cent. of zinc to the alloy from which the amalgam is made. The lower curves represent alloy F; the single curve near the top of the chart, alloy G. The preparation and the subsequent treatment of both specimens were made as nearly alike as possible. The addition of the zinc increased the heat absorption; also it increased from 77.0° to 78.1° C. the temperature at which the minimum appears in the curve of first heating.

Although differences between the amalgams are unmistakably disclosed, the contrast is by no means so striking as that brought out in Figs. 8 and

10 by the dilatometric method of thermal analysis applied to a pair of amalgams from the same alloys F and G. The differences obtained are not attributable to the fact that each cylinder of the pair examined by the thermometric method was prepared from 6 gm. alloy triturated with 1.60 times this mass of mercury for 4 min. and molded under a pressure of 400 kg. per circ. cm., while each cylinder of the pair examined by the dilatometric method was prepared from 3 gm. alloy triturated with 2.00 times this mass of mercury for 6 min. and molded under a pressure of 141 kg. per circular centimeter.

Fig. 8, as well as Fig. 16, indicates that the transition of amalgam prepared from alloy F starts at a lower temperature and proceeds more gradually the second time the specimen is heated. Likewise, in the second

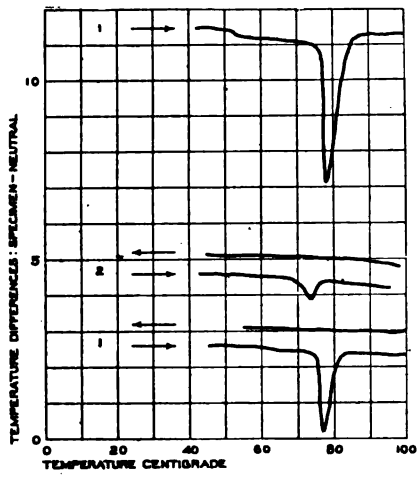

Fig. 16.

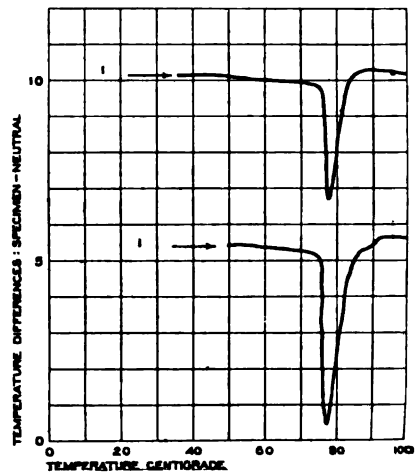

Fig. 17.

Fig. 16.—Influence of zinc; lower curves from non-zinc alloy F, top curve from zinc alloy G.

Fig. 17.—Influence of packing pressure; lower curve from amalgam of alloy E molded under 141 kg. per circ. cm., upper curve from same amalgam molded under 1131 kilogram.

curve of each figure, the minimum appears sooner and is less prominent than in the first curve.

Fig. 17 shows that increasing the packing pressure from 141 to 1131 kg. per circ. cm. reduces but little the heat absorption during the transition of an amalgam from alloy E, while it produces no clearly evident effect on either the temperature at which the sudden descent begins or the temperature at which the minimum is reached. The observed change from 77.5° to 77.2° C. is without significance.

The four alloys represented by Figs. 14, 15, and 16 were all amalgamated under the same conditions and were all packed under 400 kg. per circ. cm. The results of subjecting their amalgams to thermal

analysis afford, therefore, some information in regard to effects ascribable to variations in the compositions of the alloys. Alloys A and B both contain 5 per cent. copper and no zinc. They differ only in silver-tin ratio. Figs. 15 and 14 indicate that reducing this ratio from $^{75}/_{20}$ = 3.75 to $^{69}/_{26}$ = 2.65 makes but little change (75.0° to 74.4° C.) in the transition temperature observed on first heating. It does, however, materially lessen the reduction in heat absorption noticeable on the second curve for each alloy.

Alloys B and F do not differ widely in silver-tin ratio ($^{69}/_{26}$ = 2.65 and $^{79}/_{27}$ = 2.59). Reducing the copper content from 5 to 3 per cent. has increased from 74.4° to 77.0° C. the temperature at which the minimum appears in the curve of first heating. It has also lessened the heat absorption considerably. Upon second heating, however, no significant difference is observable in the transition temperatures of the amalgams from the two alloys: 73.7° C. for B and 73.5° for F.

Alloys B and E have the same copper content (5 per cent.), the same tin content (26 per cent.), and nearly the same silver content (69 and 68 per cent., respectively). They differ principally in that E contains 1 per cent. of zinc and B none. The amalgam from B, packed under 400 kg. per circ. cm., shows the minimum in the curve of first heating at 74.4° C. The amalgams from E, packed under 141 and 1131 kg., show the minimum at 77.5° and 77.2° C., respectively. Thus, the results from alloys B and E confirm, to some extent, those from F and G. The addition of zinc appears to raise the transition temperature.

DISCUSSION

WILMER SOUDER and CHAUNCEY PETERS, Washington, D. C. (written discussion).—The paper deals in part with the actions taking place at temperatures between 70° and 85°C. and further confirms the probable universality of the abnormal behavior of amalgams at such temperatures; but it is not likely that any amalgam filling *in situ* will receive this extreme temperature treatment.

Doctor Gray has implied that hand-packed specimens are less uniform than mechanically packed specimens, and calls attention to our variation of 12.7 per cent. in expansivity for a certain alloy *C*.[11] The larger part of this variation may well be due to a lack of uniformity of manufacturers' product since, as stated in the paper, different bottles of alloy were used for these tests. That machine-packed specimens are not homogeneous, under reasonable conditions, is shown by the 14 per cent. variation of two points on the curve of crushing strengths reported to this society two years ago by Doctor Gray.[12] (In the absence of any statement to the

[11] Transition Phenomena in Amalgams, 10.

[12] Metallographic Phenomena Observed in Amalgams. *Trans.* (1919) 60.

contrary, it is assumed that all tests are for the same alloy.) Fig. 18[13] represents crushes from a machine-packed amalgam under conditions that could possibly be reproduced in the mouth. The agreement improves somewhat in Fig. 19[14] where the mechanical packing pressure is

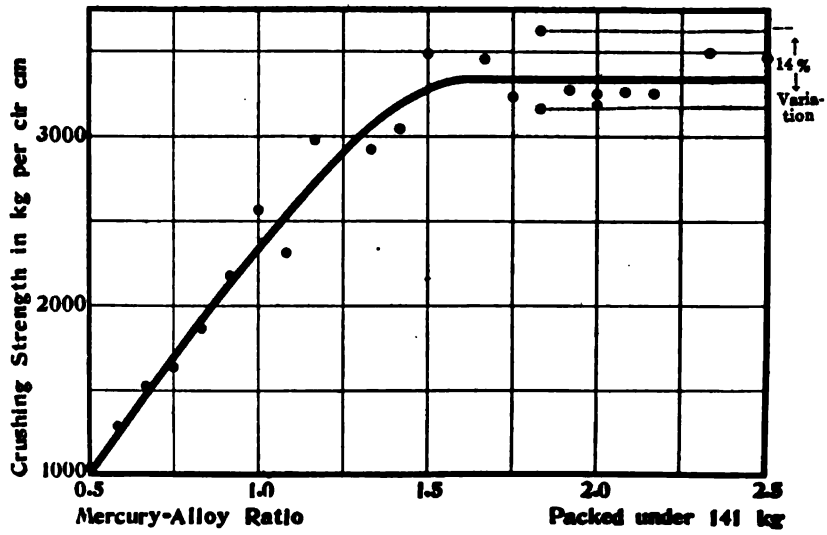

FIG. 18.—EFFECTS OF VARYING RELATIVE AMOUNTS OF MERCURY AND ALLOY THAT ARE MIXED TOGETHER IN MAKING AN AMALGAM.

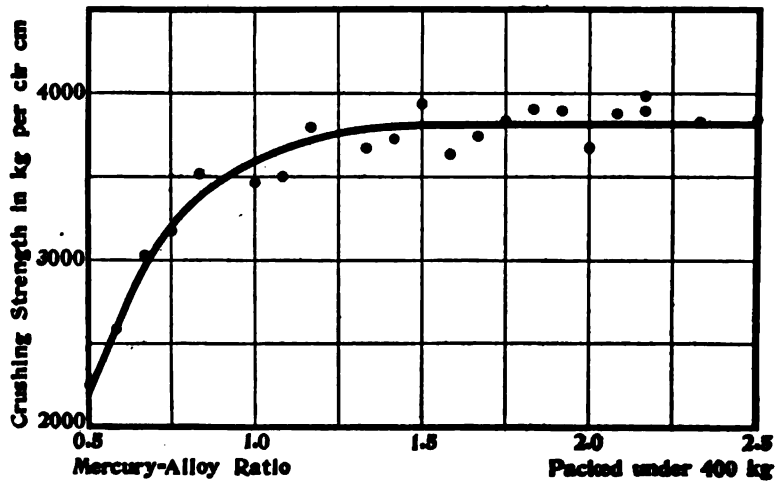

FIG. 19.—MODIFICATION OF FIG. 18 PRODUCED BY INCREASING PACKING PRESSURE FROM 141 TO 400 KG. PER CIR. CM.

far above mouth possibilities; at eight to ten times the possible mouth pressures, Fig. 20,[15] the uniformity is very much better.

[13] Fig. 7, Metallographic Phenomena Observed in Amalgams.
[14] Fig. 8, same paper. [15] Fig. 9, same paper.

This indicates that specimens packed in steel tubes with a close fitting piston, forced down with a single thrust have non-uniform spots, mercury pockets, voids, etc., unless the pressure used is approximately ten times that possible for use in the mouth.

When Doctor Gray's values for expansion are corrected by the amount indicated, they run slightly higher than ours, with perhaps a tendency to higher values for the lower mechanical packing pressures; this may be due to an over correction for the inaccuracy of his dilatometer or to the presence of mercury pockets in the specimens, mercury being an element of large expansivity. The company with which Doctor Gray is associated

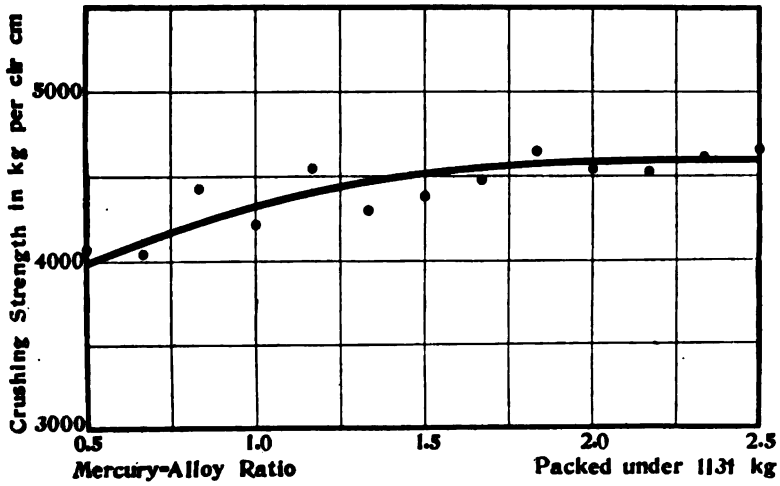

FIG. 20.—MODIFICATION OF FIGS. 18 AND 19 BY FURTHER INCREASE OF PACKING PRESSURE TO 1131 KG. PER CIR. CM.

has spent three years research in developing a set of hand-packing instruments and a technique[16] which it claims eliminates voids in the amalgams and assures a homogeneous filling. Definite instructions usually accompany each ounce of alloy; some companies specify a special set of instruments and frequently employ men to demonstrate the proper manipulation of their alloys, to secure the best results. We have secured many valuable suggestions from these representatives. In our work we attempted to comply explicitly with each reasonable detail. In the article quoted,[17] we say:

> The greatest variation in results, when using a given manipulation, appears to arise not so much from slight irregularities in manipulation of alloy as from variation in alloy from package to package. Another method of securing uniformity

[16] L. D. Caulk: *Dental Quarterly* (Feb., 1919), 20.

[17] W. H. Souder and C. G. Peters: An Investigation of the Physical Properties of Dental Materials.

of results resorted to by some investigators consists in packing specimens under continued mechanical pressure, allowing several minutes to elapse before removing them from the matrix. The authors have been more interested in finding what happens to amalgams as they are ordinarily used, or should be used.

Perhaps the impression has been left that our work on zinc content of amalgams is not definite. Those familiar with the amalgam problems know that practically all discussions on the effect of zinc have hinged on the question of the electromotive forces of zinc and non-zinc amalgams. In the light of this we include the table of values that summarizes the work on electromotive forces. From this table we may conclude that no effect need be expected due to differences of electromotive force between zinc and non-zinc alloys. The question of what takes place between gold and amalgam is far more important.

As to the effect of zinc on the transformation or critical region, we cannot attach nearly the importance given it by Doctor Gray. The fact that alloys of zinc and non-zinc "sweat" droplets at or near the critical region makes us cautious in generalizing the indicated expansivities above 60° C. These droplets sometimes crystallize, as shown by his photographs. These crystals may contain as much as 75 per cent. tin, the remainder being mercury. When one of these droplets exudes beneath a lever of the expansivity apparatus it causes this lever to indicate false, thermal expansion. As this liquid crystallizes, which it will do at falling temperatures, it separates farther the parts of the apparatus and indicates an expansion of local crystals whereas the major part of the specimen may be undergoing real contraction. Figs. 10, 11, and 12 are easily explained by this fact.

TABLE 3.—*Electromotive Force of Zinc Alloys*

Alloy	E.m.f.	Alloy	E.m.f.
0 per cent. zinc	−0.54	1 per cent. zinc	−0.52
0 per cent. zinc (duplicate)	−0.55	2 per cent. zinc	−0.52
0 per cent. zinc, 16 per cent. copper	−0.52	5 per cent. zinc	−0.51
0 per cent. zinc, 16 per cent. copper (duplicate)	−0.52	Gold (metallic)	+0.002

We have watched these drops exude beneath the contact of the interferometer. When they form at points other than those of contact, the amalgam may pass through this region with only a slight jog in the curve. Our experiments showed that it was not likely that any amalgam filling would be subjected to this high temperature; the hottest temperatures recorded in amalgams in the mouth are below this. Hence, little attention is being given to this phase of the investigation, as it does not appear to be of vital importance in dental fields.

ARTHUR W. GRAY (author's reply to discussion).—Messrs. Souder and Peters attempt to show that specimens of dental amalgams condensed in a mold by a measured pressure applied through a piston are no more uniform, under what they term reasonable conditions, than specimens packed by hand pressure with the instruments used by dentists in filling teeth. They cite two points plotted on a chart[18] published to show how the crushing strength of an amalgam is affected by varying the relative amounts of mercury and alloy that are mixed together. These points represent two cylinders that failed under crushing loads of 3627 kg. and 3167 kg., respectively. The difference between these extreme values is about 13.5 per cent. of their average.

They apparently failed to note that all the charts preceding Fig. 12 in the paper cited represent the results of preliminary tests, in which the specimens were crushed at room temperature, and both the compression and the balancing of the crushing load were regulated by hand. One of the two cylinders was made five days before the other from a different batch of alloy. Both were crushed 24 hr. after making, or before the amalgam had completely hardened. Thus, the deviation ascribed to lack of homogeneity in machine-packed amalgams may well have been due to variation in any one or more of several unknown factors, including those occasional irregularities that seem inseparable from strength tests.

If reference be made to Figs. 12 and 15 to 20 of the same paper, no such deviations will be found, although all the points in the charts represent individual specimens and no results in any series have been suppressed, even when they deviated more than usual from the averages. On the other hand, in the charts representing the preliminary tests, without temperature control and without regularity in load application, numerous examples can be found of even greater deviations than the one cited. The results of some preliminary tests were published because, in spite of their large deviations, they appeared to give sufficient evidence in regard to the phenomena that they were designed to elucidate.

As Messrs. Souder and Peters point out, the deviations of the plotted points from the curves in the three charts that they reproduce decrease with increase of packing pressure. An improvement of this kind is to be expected. But that it may not all be due to increase of packing pressure is suggested by some of the large deviations at still higher pressures plotted in Fig. 6 of the same paper. Moreover, 400 kg. per cir. cm. is not far above mouth possibilities and 1131 kg. per cir. cm. is not eight to ten times the possible mouth pressures, as Messrs. Souder and Peters assert. It is true that a pressure of 400 kg. per cir. cm., which is equiva-

[18] A. W. Gray: Metallographic Phenomena Observed in Amalgams. *Trans* (1919) **60**, 666. *Jnl.* National Dental Assn. (1919) **6**, 520.

lent to 4 kg. per cir. mm., is not usual in filling a tooth; but it is possible in small cavities favorably located.

Specimens of dental amalgams packed by piston pressure do show non-uniform spots, mercury pockets, voids, etc., especially at low packing pressures. These defects can easily be seen with a low-power microscope and often with the naked eye. To a large extent they can be obliterated by suitable manipulation of the amalgam during packing with dental instruments; but their frequent occurrence even in hand-packed amalgams can easily be verified by the examination of fillings in extracted teeth.

The various dental alloys on the market differ widely in regard to the ease with which such defects in fillings can be avoided. These differences are readily detected by observing under moderate magnification the surfaces of amalgams packed by piston with the same fairly low pressure, such as 25 or 50 kg. per cir. cm. They are most clearly revealed when sufficient time has elapsed after packing for the free mercury on the surfaces to diffuse into the interiors. Structural defects that interfere with proper adaptation of the amalgam to the walls of the tooth cavity are quite as serious as the shrinkage and flow of amalgams from low-silver alloys. A proper testing procedure will accentuate rather than conceal imperfections in a material under examination.

The packing instruments to which Messrs. Souder and Peters refer were designed to assist dentists in filling teeth. They were not designed to prepare specimens for physical tests intended to compare different dental alloys.

The condensation of amalgam test specimens by hand pressure or mallet blows is fundamentally wrong if the object be to make a reasonably accurate comparison of different dental amalgam alloys. Messrs. Souder and Peters appear to have confused testing for this purpose with testing to learn the behavior of different amalgams when employed for filling teeth. No testing method can be regarded as satisfactory until it is capable of such definite specification that different investigators will obtain essentially the same results when attempting to test the same material in accordance with the specified procedure. Dental amalgams are so sensitive to manipulation during packing that different observers get widely divergent results from hand packing the same alloy even when following the same directions. Machine packing under measured pressure *is* capable of definite specification, and yields results reproducible with fair uniformity, even as regards non-uniform spots, mercury pockets, voids, etc. Hand pressure, mallet blows, burnishing, tamping, and other dental manipulations that depend on the judgment and skill of the operator *are not* capable of definite specification.

Although mechanical packing under high pressure can be used to produce amalgam specimens considerably stronger than those produced

by dental methods of packing, it is not necessary to force up the strength in this way. Test specimens can also be prepared under packing pressures that will yield amalgam of which the strength and other characteristics will be essentially the same as obtained when dental methods are used.

Because the knowledge of such packing pressures is of great importance in furnishing a connecting link between the methods of manipulation necessary in dental practice and the methods of manipulation suitable for comparative tests of dental alloys, I have determined the mean effective dental packing pressures employed by different individuals in condensing amalgam. These range from less than 20 to more than 200 kg. per cir. cm. in packing cylindrical cavities only 3 mm. in diameter. Even in the case of a dentist possessing unusual skill in making amalgam restorations, the mean effective pressure ranged from 62 to 234 kg. Larger cavities, such as those used by Messrs. Souder and Peters, while easier to pack mechanically, are still more difficult to pack by hand.

Messrs. Souder and Peters do not indicate how they determined "possible mouth pressures." The mean effective dental packing pressure cannot be computed from measurements of the operator's hand thrust and the area of the packing instrument used. Since it depends on several other factors, including the size of the cavity and the nature of the amalgam, it must be determined experimentally. For this purpose, use may be made of variations in any property that can be expressed as a known function of the packing pressure, such as strength, mercury content, density, or reaction expansion.

In the cases cited, the mean effective pressure was determined by application of the logarithmic law connecting crushing strength with packing pressure.[19] The specimens were all crushed when within one degree of 37.5° C. and corrections were applied for any deviations from this temperature. For determining the constants in the equation, a pair of test cylinders were packed under each of the following pressures: 100, 200, 400, 800, and 1600 kg. per cir. cm. The crushing strength found for each cylinder differed from the average for the pair by 1.1, 0.2, 2.6, 2.0, and 1.3 per cent., respectively, the average being 1.4 per cent.

Thirteen specimens of the same amalgam were packed by hand in the same mold with dental instruments; each of four individuals, using the same instruments, packed from one to five specimens as well as he could. The average deviation from the average crushing strength was 7.6 per cent. of this average; the difference between the highest and the lowest value was 34 per cent. The average value of the mean effective packing pressure was 68 kg. per cir. cm.; the average deviation from this was 64

[19] *Trans.*, 664; *Jnl.* N. D. A., 518.

per cent.; the difference between the highest (234 kg.) and the lowest (17 kg.) was 321 per cent. Do these results indicate that hand-packed specimens are more reliable than machine-packed ones for the purpose of comparing different dental amalgam alloys?

In trying to account for their variation of 12.7 per cent. in the thermal expansivity of a certain alloy, Messrs. Souder and Peters assert that "the larger part of this variation may well be due to a lack of uniformity of manufacturers' product since, as stated in the paper, different bottles of alloy were used for these tests;" and again, that "the greatest variation in results, when using a given manipulation, appears to arise not so much from slight irregularities in manipulation of alloy as from variations in alloy from package to package." This explanation is plausible, but it is not valid. They submit no data to show that their experimental technique is sufficiently reliable to yield substantially the same result whenever a given test is repeated with samples of alloy from the same package. They have failed to control either packing pressure or temperature, both of which exert considerable influence upon the behavior of a dental amalgam.[20] At body temperature, a change of 1° C. changes the crushing strength approximately 50 kg. per cir. cm., or 900 lb. per sq. in. If neither temperature nor packing pressure is controlled, what significance can be attached to variations of a few thousand pounds per square inch in the results of crushing tests? Messrs. Souder and Peters have published results to 50 lb. per sq. in., notwithstanding such fluctuations due to temperature alone.[21]

As a matter of fact, numerous tests of dental alloys fail to show any such lack of uniformity as Messrs. Souder and Peters assume. Some alloys are, indeed, defective, especially as regards annealing. Some manufacturers, recognizing that their products change with age, date the packages and inform the dentist that alloy more than a year old should be exchanged for fresh material.

The correction that Messrs. Souder and Peters have ascribed to the inaccuracy of my dilatometer is a correction of exactly the same nature as the one they apply to their own measurements because of the expansion of the base of their interferometer, and which they designate by Cs in equation (4).[22] Since my reference material was invar instead of glass, my correction was only about one-tenth (or perhaps only about one-twentieth) of the correction necessary with the interferometer. For my purposes a closer knowledge of the expansivity did not warrant the labor involved in a special determination.

[20] Ibid.

[21] Table 3, entitled "Comparison of Amalgams," *Dental Cosmos* (1920) **62**, 332-334; Bureau of Standards *Tech. Paper* 157 (1920) 38.

[22] *Dental Cosmos* (1920) **62**, 312; Bureau of Standards *Tech. Paper* 157, 13.

The claims that have been made in regard to the effect of zinc on a dental amalgam have by no means been confined to its alleged effect on electromotive force. This particular claim is of recent origin, and has been exploited mainly, if not solely, in connection with advertising propaganda. Measurements made by the writer early in 1917 showed that zinc produced but little effect on the electromotive force developed between gold and amalgam, either in the mouth or in various electrolytes. The results published by Messrs. Souder and Peters confirm these observations.

Messrs. Souder and Peters do not make clear how Figs. 10 and 11 are easily explained by an expansion of local crystals during their formation at falling temperatures, since both of these figures show the abnormal expansion at constant or slowly rising temperatures.

They certainly would not insist that the phenomena I have recorded are of no importance in dental fields. Failure to show immediate practical applications does not necessarily mean that the information disclosed may not lead to new developments, or that it is without interest to metallographists.

Physical Tests on Sheet Nickel Silver

By Wm. B. Price,* Ph. B., and Philip Davidson,† M. S., Waterbury, Conn.

(Columbus Meeting, October, 1920)

The object of this paper is to present a survey of some of the physical properties of sheet nickel silver when subjected to cold rolling and when annealed at temperatures extending from 350° C. throughout the commercial annealing range.

A number of alloys were taken from stock and analyzed. Four of these, representing low nickel and high nickel both with and without lead, were chosen for the tests. The analyses were as follows:

Alloy	Copper, Per Cent.	Lead, Per Cent.	Iron, Per Cent.	Nickel, Per Cent.	Manganese, Per Cent.	Zinc, Per Cent.
A.....	64.68	Trace	0.194	6.73	0.06	remainder
B.....	65.82	1.27	0.227	6.17	0.06	remainder
C.....	65.44	Trace	0.345	17.83	0.08	remainder
D.....	65.60	1.08	0.238	17.77	0.06	remainder

These alloys were rolled in accordance with regular mill practice to approximately No. 6 B. & S. gage. The bars (which were then coiled) were annealed together in a mill muffle and afterwards pickled in a 10 per cent. sulfuric-acid solution and cold rolled in stages of approximately one number (B. & S.) at a time to No. 18 B. & S. gage. After each stage, suitable samples were set aside for physical tests. Additional samples were chosen for tests after the bars were rolled to Nos. 8, 10, 12, and 14 gage. These samples were annealed together in the mill muffle and, after pickling, were finished on 0.050-in. gage, yielding a series of specimens 2, 4, 6, and 8 numbers hard for the subsequent annealing tests.

Tensile test pieces 9 by 1 in. (22.9 by 2.5 cm.) were cut from both lots and the central portion was milled to give a test section 2½ in. long by ½ in. wide. A distance of 2 in. was marked off on the edge of each specimen with light punch marks. In the case of the annealed alloys, Erichsen test pieces 4 by 2½ in. were also taken.

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Methods of Testing

The tensile tests were made on a 50,000-lb. Olsen testing machine adjusted to take a maximum load of 5000 lb. (2268 kg.). The yield point was considered to be that load necessary to produce a permanent set of 0.001 in. in 2 in. and was obtained by measuring the elongation of the specimen during the test with a pair of dividers. The Brinell tests were made with an Olsen hydraulic machine, as preliminary tests on the tensile test pieces. A pressure of 500 kg. for 30 sec. with a 10-mm. ball was used. The scleroscopic hardness tests were also made on the tensile test pieces using the Shore universal hammer. The Erichsen ductility tests were made with a machine equipped with standard Erichsen tools but so designed that the pressure required to produce a cup was measured on the Olsen testing machine. The advantages of such a machine over the standard Erichsen machine are: the speed of cupping can be made uniform, the end point is sharp, and the load necessary to cup the material can be measured with precision.

Specimens for microstructure were also taken from the ends of the test specimens before pulling. Alloys A and B were etched with $NH_4OH + H_2O_2$, while dilute acidified ferric chloride solution was used in the case of alloys C and D. All micrographs were made at a magnification of 75 diameters.

Results of Tests on Rolled Specimens

The results of the physical tests made on the rolled specimens are shown in Tables 1 and 2; they are represented graphically in Figs. 1 and 2. Representative micrographs of alloys A and C are shown in Figs. 9 and 10.

The curves show that, in a general way, the alloys with the lower nickel content are slightly harder than brass subjected to similar treatment. The alloys with the higher nickel content, however, although slightly harder when in the annealed condition, do not harden as rapidly under severe cold rolling as those with the lower nickel content. The comparison is shown graphically in Fig. 3. As a matter of fact, in works practice alloys with the higher nickel content are considered more amenable to cold working operations than those with the lower nickel content. The presence of about 1 per cent. of lead in either alloy does not appear to affect the physical properties to any great extent.

Physical Tests on Annealed Strips

As stated, samples approximately 2, 4, 6, and 8 numbers (B. & S.) hard at 0.050-in. (1.27-mm.) gage were obtained from each of the four alloys.

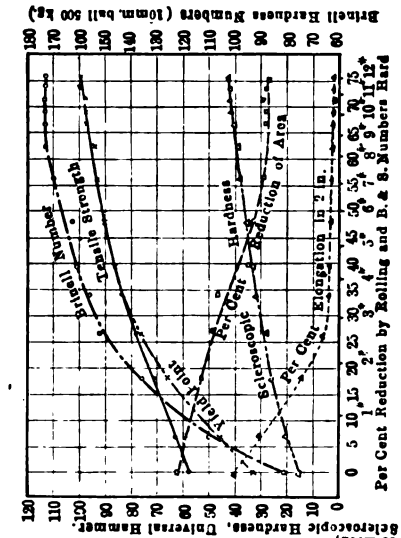


FIG. 2.—PHYSICAL TESTS ON COLD-ROLLED MATERIAL. ALLOY C.

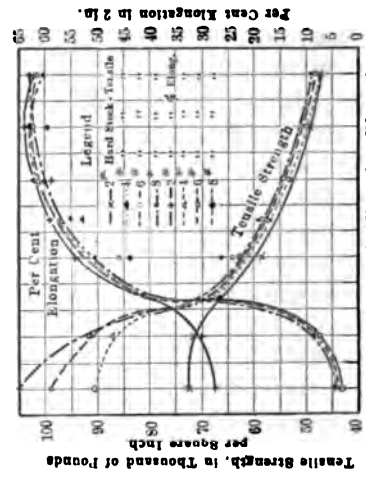


FIG. 4.—PHYSICAL TESTS TAKEN ON ANNEALED MATERIAL. ALLOY A. ORIGINAL SAMPLES REDUCED 19.55, 44.4, 51.9, AND 60.5 PER CENT.

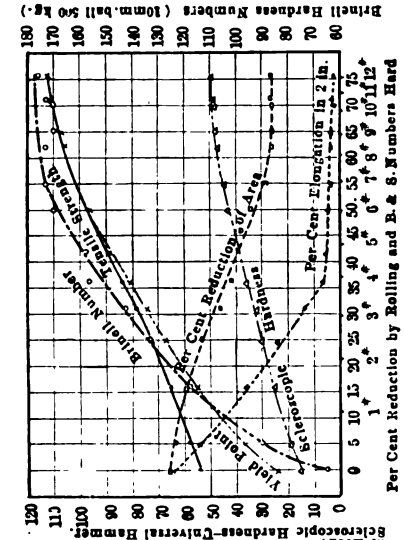


FIG. 1.—PHYSICAL TESTS ON COLD-ROLLED MATERIAL. ALLOY A.

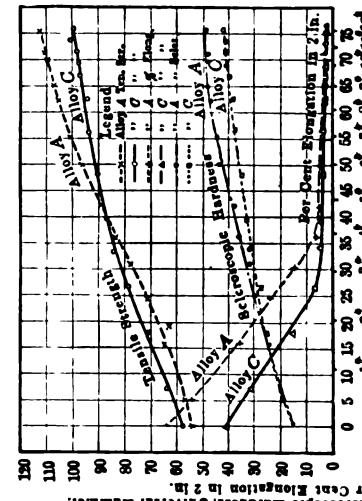


FIG. 3.—COMPARISON OF PHYSICAL PROPERTIES OF COLD-ROLLED ALLOYS A AND C.

Three tensile and three Erichsen specimens from each lot (making 48 tensile and 48 Erichsen specimens) were placed on a small pan 11 by 14 in. (28 by 36 cm.) and carefully annealed in a nichrome-wound

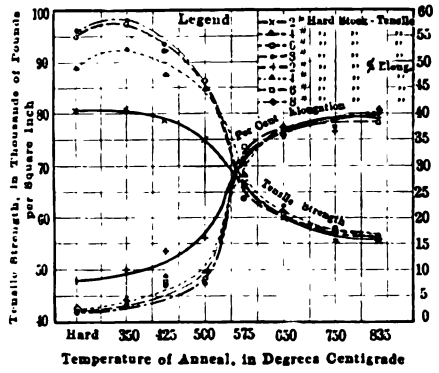


FIG. 5.

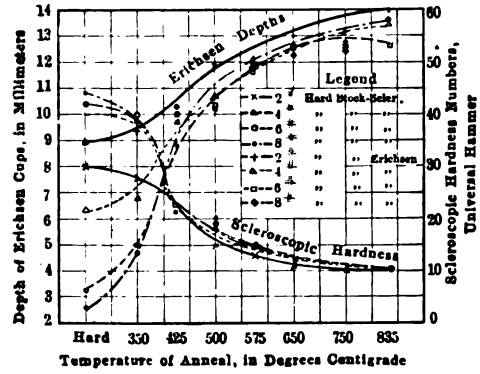


FIG. 6.

FIG. 5.—PHYSICAL TESTS TAKEN ON ANNEALED MATERIAL. ALLOY C. ORIGINAL SAMPLES REDUCED 16.6, 40.3, 52.7, AND 62.0 PER CENT.

FIG. 6.—ERICHSEN DUCTILITY AND SCLEROSCOPIC HARDNESS TESTS TAKEN ON ALLOY A, ANNEALED SERIES.

electric muffle furnace 12 in. wide by 8 in. high by 28 in. deep, the temperature of which was controlled by means of a Pt-Pt-Rh thermocouple used in conjunction with an Englehardt millivoltmeter. The specimens were annealed for ½-hr. periods at the temperature designated, plus a

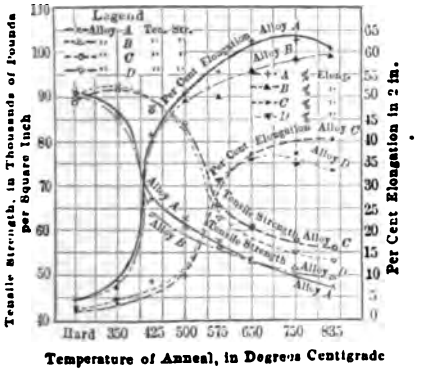


FIG. 7.

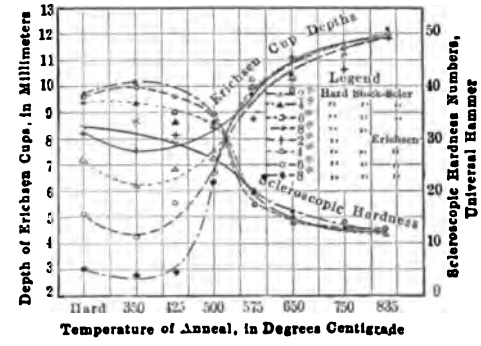


FIG. 8.

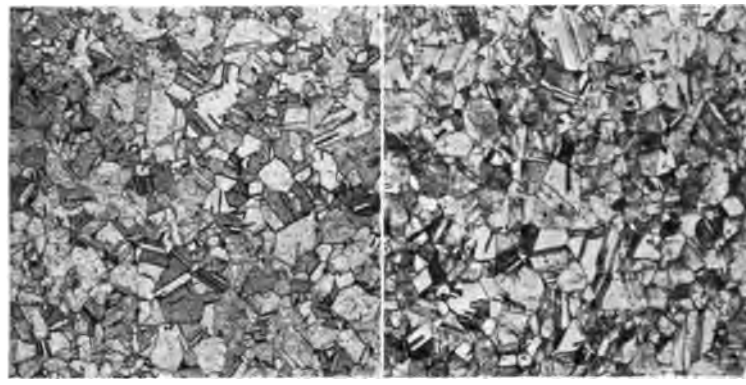
FIG. 7.—TENSILE STRENGTH AND PER CENT. ELONGATION OF ANNEALED SAMPLES ALLOYS A, B, C, AND D PREVIOUSLY ROLLED 4 NUMBERS HARD.

FIG. 8.—ERICHSEN DUCTILITY AND SCLEROSCOPIC HARDNESS TESTS TAKEN ON ALLOY C, ANNEALED SERIES.

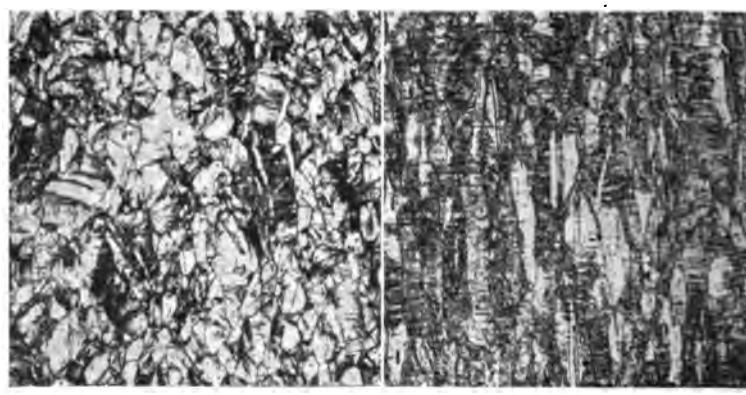
preheating period averaging 1 hr. 17 min. The physical test results are given in Tables 3 to 10. The tensile test values are shown plotted against the temperature in Figs. 4 and 5.

The Erichsen ductility values and the scleroscopic hardness values are shown in plotted form in Figs. 6 and 8; these curves are similar to the tensile strength and elongation curves in Figs. 4 and 5. The Erichsen curve parallels the per cent. elongation curve while the scleroscopic hardness curve is similar to the tensile strength curve.

The grain characteristics of nickel silver are similar to those of brass, except that grain growth is retarded by the presence of nickel. The



a. MILL ANNEAL. *b.* 16.18 PER CENT. REDUCTION.



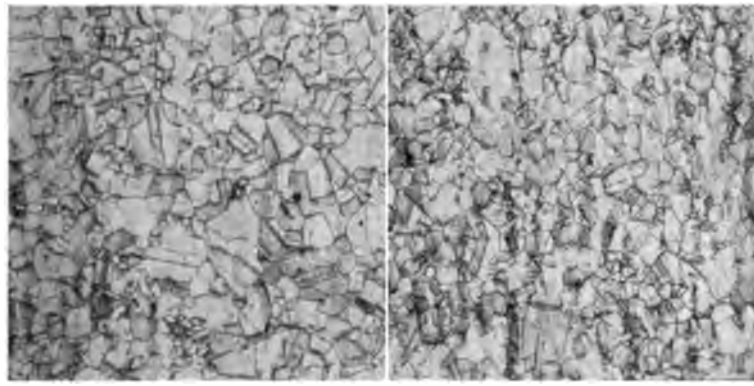
c. 41.74 PER CENT. REDUCTION. *d.* 75.41 PER CENT. REDUCTION.

FIG. 9.—ROLLED SERIES, ALLOY A. ETCHED IN $NH_4OH + H_2O_2$. × 75.

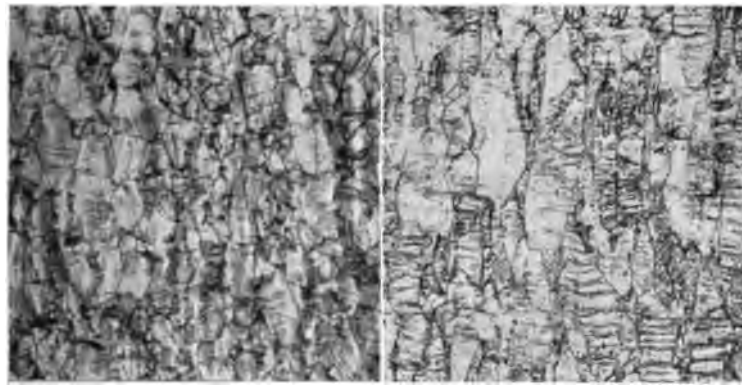
severely worked material with the lower nickel content, alloys A and B, shows a beginning of recrystallization at 350° C., which is 50° C. higher than in the case of alpha brass. The first signs of recrystallization on the hard-rolled specimens of the higher nickel content, alloys C and D, are observed at 500° C. The great differences in tensile strength, per cent. elongation, etc., seen in the samples reduced various amounts by rolling

are approximately equalized by an anneal at 425° C., in the case of alloys A and B, and at 575° C., with alloys C and D.

The comparative properties of the four alloys are shown in Fig. 6, which gives the annealing characteristics of material originally four numbers hard. It will be seen that the effect of nickel is to raise the tensile strength and lower the per cent. of elongation. The specifically higher initial strength and lower elongation are evidently not unfavorable



a. MILL ANNEAL. *b.* 17.75 PER CENT. REDUCTION.



c. 47.97 PER CENT. REDUCTION. *d.* 76.0 PER CENT. REDUCTION.

FIG. 10.—ROLLED SERIES, ALLOY C. ETCHED IN $FeCl_3$. × 75.

from the cold working standpoint, as indicated by the behavior of the metal when subjected to severe reduction by rolling.

MICROSTRUCTURE

Representative micrographs of the structures of alloys A and C, originally about six numbers (B. & S.) hard, are shown in Figs. 11 and

12. Plate (*b*) Fig. 11 shows, for alloy A, incipient recrystallization after an anneal at 350° C.; at 425° C., the recrystallization is complete. The grains grow as the temperature rises but they are consistently smaller than those of brass treated in a similar way. These photomicrographs illustrate clearly that, in order to attain a given grain size, the 18 per cent. nickel silver requires an annealing temperature from 100 to 150° C. higher than the 7 per cent. alloy.

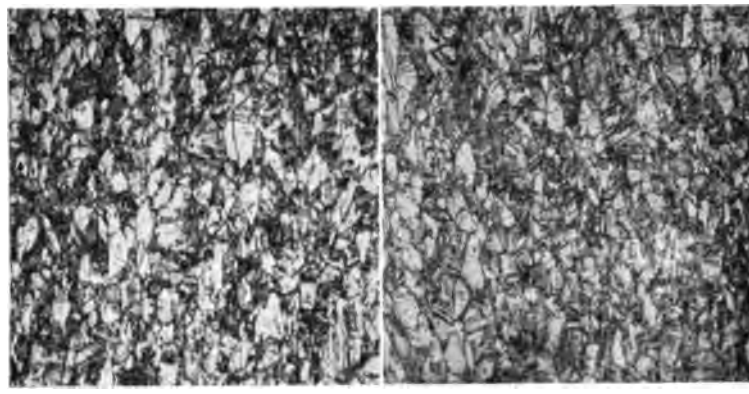
TABLE 1.—*Physical Tests on Cold-rolled Material, Alloy A**

Gage	Reduction by Rolling, Per Cent.	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Scler. Hardness	Brinell Number
0.1545		24,666	53,767	64.5	65.7	15.0	65
0.1465	5.17	37,233	57,467	54.7	63.0	19.0	90
0.1295	16.18	54,933	64,533	35.8	59.5	25.0	118
0.1165	24.59	67,400	71,400	23.7	53.1	30.0	132
0.1065	31.06	74,000	77,800	13.3	46.3	32.0	142
0.0985	36.24	80,733	83,267	6.8	42.3	36.0	156
0.0900	41.74	84,550	88,733	5.8	39.1	38.0	158
0.0775	49.83	96,367	96,367	4.7	34.1	43.0	170
0.0645	58.25	101,500	101,500	3.5	28.5	44.0	173
0.0585	62.13	105,533	105,533	3.2	26.2	47.0	173
0.0540	65.04	106,867	106,867	3.2	26.2	48.0	170
0.0465	69.90	109,733	109,733	2.5	26.3	48.0	170
0.0445	71.19	110,967	110,967	2.8	26.6	48.5	174
0.0380	75.41	112,300	112,300	2.5	26.5	49.0	176

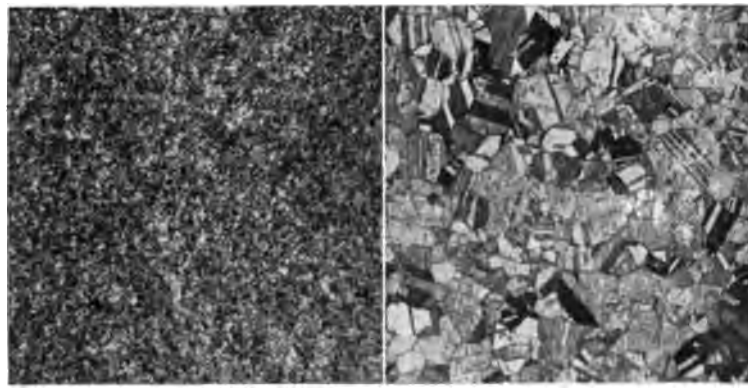
TABLE 2.—*Physical Tests on Cold-rolled Material, Alloy C**

Gage	Reduction by Rolling, Per Cent.	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Scler. Hardness	Brinell Number
0.1605		33,033	58,133	40.2	62.5	15.8	82
0.1490	7.16	46,900	63,100	31.2	59.6	20.3	110
0.1320	17.75	66,267	70,800	14.7	52.8	26.0	136
0.1175	26.79	76,733	78,333	6.5	48.7	28.0	152
0.1060	33.95	81,300	84,067	4.3	46.7	32.0	156
0.0970	39.56	86,367	86,367	3.7	34.9	33.0	161
0.0835	47.97	90,133	90,133	3.2	33.3	35.0	163
0.0700	56.38	93,633	93,633	3.2	29.4	38.0	170
0.0605	62.30	94,133	94,133	2.7	27.6	39.0	173
0.0535	66.66	97,333	97,333	2.5	28.3	40.0	173
0.0495	69.15	97,500	97,500	2.2	28.2	42.0	173
0.0460	71.33	97,900	97,900	1.5	29.1	42.0	173
0.0425	73.52	100,500	100,500	2.3	27.7	42.0	173
0.0385	76.01	99,767	99,767	2.0	27.2	43.0	173

* These are the average results obtained on three samples.

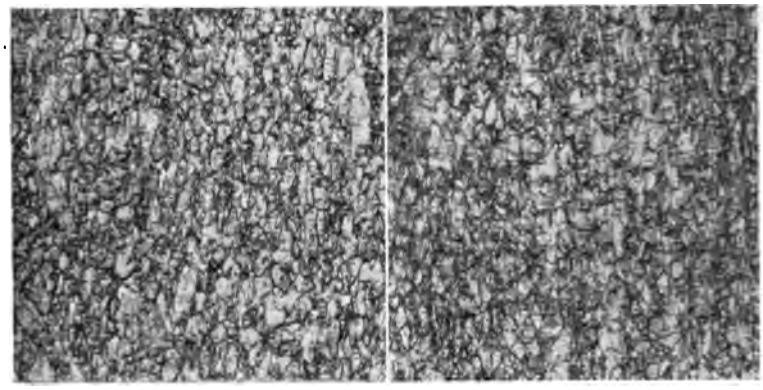


a. 51.9 PER CENT. REDUCTION. *b.* ANNEALED AT 350° C.

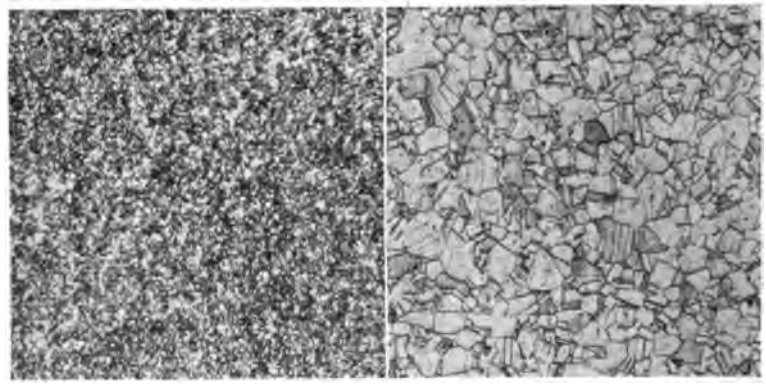


c. ANNEALED AT 425° C. *d.* ANNEALED AT 650° C.

FIG. 11.—ANNEALED SERIES, ALLOY A. ETCHED IN $NH_4OH + H_2O_2$. × 75.



a. 52.7 PER CENT. REDUCTION. *b*. ANNEALED AT 425° C.



c. ANNEALED AT 575° C. *d*. ANNEALED AT 750° C.

FIG. 12.—ANNEALED SERIES, ALLOY C. ETCHED IN $FeCl_3$. × 75.

TABLE 3.—*Physical Tests on Annealed Material, Alloy A**

Original Sample Reduced 19.55 Per Cent. by Rolling

Treatment	Yield Point Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent	Erichsen			Scler. Hardness
					Press. Pounds	Press. Pounds per mm.	Cup Depth, mm.	
Original Sample	53,267	72,667	27.8	49.3	5,263	586	8.97	30
350° C.	64,133	71,800	30.2	45.1	5,311	563	9.47	28
425° C.	45,866	66,100	39.8	52.7	5,573	636	8.76	22
500° C.	31,433	59,167	54.3	52.8	6,393	535	11.94	15
575° C.	26,667	56,700	59.2	54.6	6,364	528	12.07	13
650° C.	22,633	53,200	58.5	55.7	6,214	479	12.96	12
750° C.	20,633	49,133	64.0	54.3	5,796	451	12.85	10
835° C.	18,533	46,967	62.5	50.4	5,569	399	13.97	10

TABLE 4.—*Physical Tests on Annealed Material, Alloy A**

Original Sample Reduced 44.4 Per Cent. by Rolling

Treatment	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Erichsen			Scler. Hardness
					Press, Pounds	Press. Pounds per mm.	Cup Depth, mm.	
Original Sample	90,433	90,433	4.8	35.4	4,485	709	6.33	40
350° C.	82,267	87,100	8.5	33.7	4,576	673	6.80	39
425° C.	44,967	66,667	41.5	47.4	6,047	621	9.74	21
500° C.	38,000	62,567	50.7	49.2	6,294	591	10.66	18
575° C.	28,267	57,633	55.25	53.0	6,068	512	11.85	15
650° C.	22,033	53,367	62.0	55.5	5,689	453	12.57	11
750° C.	22,400	49,433	62.8	54.5	5,504	422	13.03	10
835° C.	17,667	47,400	60.3	53.2	5,320	397	13.39	10

* These are the average results obtained on three samples.

LE 5.—*Physical Tests on Annealed Material, Alloy A**

Original Sample Reduced 51.9 Per Cent. by Rolling

Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Erichsen			Scler. Hardness
				Press. Pounds	Press., Pounds per mm.	Cup Depth, mm.	
99,167	99,167	3.5	29.5	2,140	645	3.33	42
77,550	91,850	6.8	31.8	3,835	771	4.98	40
44,900	67,900	41.2	49.6	6,383	638	10.01	22
40,133	64,267	46.2	51.0	6,271	607	10.33	19
28,367	57,733	57.0	51.7	6,053	520	11.66	15
22,567	53,833	61.5	56.1	5,978	479	12.49	12
21,033	49,933	62.3	53.5	5,588	438	12.75	10
19,800	48,333	62.0	53.6	5,377	404	12.66	10

LE 6.—*Physical Tests on Annealed Material, Alloy A**

Original Sample Reduced 60.5 Per Cent. by Rolling

Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Erichsen			Scler. Hardness
				Press., Pounds	Press., Pounds per mm.	Cup Depth, mm.	
104,967	104,967	4.2	27.9	1,664	641	2.60	44
74,767	91,133	8.8	34.5	3,704	760	4.87	40
48,200	69,667	41.5	47.8	6,516	631	10.33	23
42,800	66,333	44.2	48.2	6,543	636	10.29	20
29,067	58,400	55.3	54.4	6,419	538	11.92	15
21,633	53,666	62.7	56.9	6,180	499	12.38	12
19,933	50,067	59.7	54.2	5,825	463	12.57	10
20,233	48,867	63.7	54.4	5,611	414	13.55	10

* These are the average results obtained on three samples.

TABLE 7.—*Physical Tests on Annealed Material, Alloy C**

Original Sample Reduced 16.6 Per Cent. by Rolling

Treatment	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Erichsen			Scler. Hardness
					Press., Pounds	Press., Pounds per mm.	Cup Depth, mm.	
Original Sample	67,000	80,766	8.0	40.7	4,712	574	8.21	32.0
350° C.	77,900	80,933	9.8	39.9	4,750	632	7.52	33.0
425° C.	70,233	78,433	13.7	40.0	4,875	604	8.07	29.0
500° C.	65,500	75,000	16.0	43.75	4,837	577	8.38	27.5
575° C.	46,566	66,660	30.7	44.6	4,865	553	8.80	20.0
650° C.	29,000	59,933	37.5	44.9	5,535	502	11.03	15.0
750° C.	24,067	55,567	37.3	45.7	5,433	498	10.92	14.0
835° C.	21,100	55,867	39.3	45.7	5,490	463	11.87	12.0

TABLE 8.—*Physical Tests on Annealed Material, Alloy C**

Original Sample Reduced 40.3 Per Cent. by Rolling

Treatment	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Erichsen			Scler. Hardness
					Press., Pounds	Press., Pounds per mm.	Cup Depth, mm.	
Original Sample	88,933	88,933	2.3	30.9	4,434	617	7.19	37
350° C.	89,600	92,300	4.2	33.7	4,248	693	6.13	37
425° C.	83,800	87,700	8.7	35.0	4,517	663	6.82	33
500° C.	79,300	84,567	9.8	38.9	4,499	629	7.17	33
575° C.	42,533	65,967	28.7	45.5	5,275	528	10.01	20
650° C.	30,667	61,067	37.0	49.8	5,142	504	10.21	15
750° C.	24,000	57,700	37.2	42.5	5,358	471	11.37	13
835° C.	21,767	55,900	40.3	44.6	5,237	434	12.06	12

*These are the average results obtained on three samples.

TABLE 9.—*Physical Tests on Annealed Material, Alloy C**

Original Sample Reduced 52.7 Per Cent. by Rolling

Treatment	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Erichsen			Scler. Hardness
					Press., Pounds	Press., Pounds per mm.	Cup Depth mm.	
Original Sample	95,000	95,000	2.3	30.8	3,555	688	5.16	38
350° C.	89,533	97,533	3.7	31.0	2,444	639	3.82	40
425° C.	87,133	91,667	7.7	35.3	3,932	710	5.56	35
500° C.	78,800	86,000	8.5	37.9	4,423	657	6.73	35
575° C.	39,333	64,266	34.3	49.3	5,418	534	10.15	18
650° C.	29,350	60,950	36.8	44.9	5,147	521	9.88	14
750° C.	26,750	57,800	37.8	44.7	5,300	473	11.21	14
835° C.	22,900	56,250	38.5	47.3	5,304	447	11.94	13

TABLE 10.—*Physical Tests on Annealed Material, Alloy C**

Original Sample Reduced 62.0 Per Cent. by Rolling

Treatment	Yield Point, Pounds per Square Inch	Tensile Strength, Pounds per Square Inch	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.	Erichsen			Scler. Hardness
					Press., Pounds	Press., Pounds per mm.	Cup Depth, mm.	
Original Sample	96,167	96,167	2.0	29.3	2,012	665	3.03	39
350° C.	96,633	98,333	3.2	30.5	1,794	642	2.79	41
425° C.	86,867	93,533	7.3	34.7	2,038	699	2.93	38
500° C.	80,200	85,933	8.2	37.5	4,316	685	6.30	35
575° C.	43,867	65,933	31.7	44.6	5,360	549	9.78	20
650° C.	34,300	62,067	36.3	44.3	5,420	526	10.30	16
750° C.	24,567	57,100	37.7	45.5	5,483	482	11.37	13
835° C.	22,067	56,167	39.8	43.6	5,368	442	12.15	12

* These are the average results obtained on three samples.

DISCUSSION

W. R. WEBSTER,* Bridgeport, Conn.—The statement that "The presence of about 1 per cent. of lead in either alloy does not appear to affect the physical properties to any great extent," may be misunderstood. It is well known that the addition of lead materially affects the cutting qualities of the material. Then again, it has some sort of an effect which has not been studied very carefully as yet on the physical properties of the material at high temperatures; that is, temperatures below the melting point and more particularly in the range of so-called "black" heats.

PHILIP DAVIDSON.—The leaded-nickel silvers were treated exactly the same as the non-leaded, so far as rolling and annealing are concerned. We annealed the leaded-nickel silver alloys from 350° to 830° C. and the crystal growth was retarded somewhat by the presence of the lead. At 830° the metal did not seem to deteriorate; the crystals were not so large as to spoil the tensile strength or the per cent. of elongation. The lead affects the machining but we dealt more with the physical properties, so far as tensile strength and elongation are concerned.

Lead makes the metal more sensitive to fire and water-cracking; that is, metal containing lead, if heated red and plunged suddenly into cold water, will crack.

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* Bridgeport Brass Co.

Colloidal State in Metals and Alloys

By Jerome Alexander,* M. Sc., New York, N. Y.

(Columbus Meeting, October, 1920)

The object of this paper is to show that many of the important phenomena of metals and alloys are due to the facts that, at some stage, metals and alloys, or some of their constituents, are in a colloidal state and that a portion of the metal or alloy tends to remain in this state. The so-called amorphous phase in pure metals is an isocolloid, consisting of colloidal groups of metal molecules that may be dispersed in still more finely subdivided metal; these colloidal particles are not truly amorphous, but may consist, in part, if not entirely, of ultramicroscopic crystals; as a result the expressions amorphous phase and amorphous theory might be replaced by the expressions colloidal phase and colloidal theory.

Any substance is in the colloidal state when the constituent particles consist of molecular or atomic groups, whose size varies approximately from about 100$\mu\mu$ down to about 5$\mu\mu$, that is from just below the limit of microscopic resolvability to the dimensions commonly ascribed to the larger molecules. Colloidality involves no assumption as to the shape, internal structure, or orientation of the colloidal particles; *size alone is the critical factor.* A colloidal system may therefore contain crystalline groups, or amorphous groups (non-crystalline, random or haphazard clusters), or a mixture of the two.

All colloids consist of at least two phases, the subdivided substance, or dispersed phase, and the substance into which this is subdivided, the dispersion medium. It is not necessary that there be any chemical difference between the dispersed phase and the dispersion medium. As molecular forces are extremely powerful, their application may produce marked changes in the physical properties of metals. It is doubtful whether metal in the interior, especially of large masses, possesses the same properties as that on or near the surface, which alone is open to inspection.

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* Member, Committee on the Chemistry of Colloids, National Research Council. Treasurer and Chemist, National Gum & Mica Co. and National Glue & Gelatine Works.

Isocolloids and Allocolloids

When a substance is colloidally dispersed in another form of itself, it constitutes an isocolloid; *i.e.*, water droplets in condensing steam (Wo. Ostwald). Isocolloids may consist of a single element, in which case the dispersed and the dispersing phases are usually regarded as different allotropic forms of the element in question. Ostwald has proposed the term allocolloids for such systems, of which sulfur, selenium, and phosphorus are typical examples. The relation to alpha, beta, and gamma iron will at once occur to metallographists.

Effect of Changes in Molecular Forces on Physical Properties of Metals

When a metal is heated to fusion, the thermal agitation of its molecules is sufficient to overbalance, at least to some extent, the mutual attraction of its molecules; but this does not mean that the strong aggregation tendency of its molecules is without effect. On the contrary, in the state of kinetic equilibrium that exists, there must be a number of molecular groups, the size and number of which tend to increase as the solidification point is approached; that is, as the thermal agitation diminishes. The higher the temperature to which the metal is heated and the more quickly it traverses the zone of intense thermal agitation to the comparative quiet of solidification, the smaller and more numerous will be the molecular groups. The general tendency seems to be for atoms or simple molecules to form crystals, whereas complicated molecules, especially those with several foci of attraction (like gelatine, etc.), tend to remain in random or colloidal clusters. Although Traube's experiments[1] indicate that liquid zinc, cadmium, and mercury are monatomic, investigation will probably show that all metals, and especially those with high melting points, exhibit molecular association or allotropism near their freezing points.

It would appear, then, that just prior to solidification and crystallization, all pure metals are isocolloids. But the powerful molecular attractive forces act so rapidly that, as a general rule, the major portion of the metal forms macroscopic or microscopic crystals, which are embedded in an intercrystalline network of, mainly, colloidally dispersed metal having different physical properties from the crystals. While a fluid metal may contain a percentage of isolated molecules, it does not seem possible that many of these remain in the solidified metal, which consists mainly of macro- and microcrystals, and of oriented and unoriented groups of colloidal dimensions. Thus not even the most rapid chilling

[1] *Berichte* (1898) **31**, 1562. W. E. S. Turner: "Molecular Association," 53. N. Y., 1915. Longmans, Green & Co.

prevents non-magnetic γ iron from becoming magnetic, although at the temperature of transformation the metal is no longer fluid.

Effects of Rapid Chilling on the Physical Properties of Metals

The more rapidly the fused metal is chilled, the less opportunity is there for the growth of crystals beyond the colloidal stage—it is well known that quick cooling yields fine structure. The effect of quick chilling on the hardness and specific gravity of metals is illustrated by the following results, kindly worked out by Mr. W. A. Cowan of the National Lead Company's research laboratory on pieces 2 in. in diameter and 1 in. high. The chill castings were made in a water-jacket cylindrical mold, but the slowly cooled specimens were cast in a hot mold and required 12 min. to solidify when cast from a moderate temperature. Small vertical sections, weighing about 20 gm., were cut radially from the test pieces, and the specific gravity of these was determined by immersion in distilled water, with weighings before and after. Before making the hardness tests, both sides of the specimens were machined flat, $\frac{1}{16}$ in. being removed from the bottom for testing surfaces. The results are as follows:

	Specific Gravity $\frac{23}{4}$	Brinell Hardness Numbers
Tin (Straits) chill cast	7.309	8.8
slowly cooled	7.301	7.7
Lead (corroding) chill cast	11.367	5.2
slowly cooled	11.354	4.4

As the differences between the melting and chilling temperatures in these experiments are rather narrow, tests will be made in which liquid air is the chilling medium. The results of quick chilling are analogous to those of cold hammering, which shatters the large grains and increases the percentage of colloidal metal present. Zay Jeffries[2] reports the following results:

	Brinell Hardness Numbers
Cast tin, large grain	9.12
Cold hammered tin	11.32
Cast lead, large grain	5.44
Cold hammered lead	6.54

Much regarding the minute structure of metals may be determined by metallography, which involves the microscopic examination of suitably polished and etched metallic surfaces. Of the so-called amorphous, or colloidal, phase, however, metallography can tell us little outside of its

[2] *Jnl.* Am. Inst. Metals (1917) **11**, 318.

occurrence and distribution. Owing to the great opacity of solid metals, it has been impossible to subject the colloidal phase to successful ultramicroscopic examination, and such examination of thin films presents difficulties and cannot be applied to the mass, although it may be of interest. Glass, however, may be readily examined ultramicroscopically, and a consideration of the phenomena observed in glasses will give some insight into what occurs in metals and alloys.[3] Among glass technologists a molten batch of glass is called "metal," a term remarkably well chosen, for there are numerous analogies between glasses and most metals; but there are, of course, many enormous and marked differences even in their analogous properties.

Factors Controlling Behavior of Supercooled Melts

As Tammann has shown,[4] three main factors control the behavior of supercooled melts: the specific crystallization capacity, which is measured by the number of centers of crystallization formed in a unit mass in a unit time; the speed of crystallization; and the variation in viscosity. In various mixtures of fused silicates composing molten glasses, the viscosity increases so rapidly upon cooling that the crystallization forces are unable to establish themselves before the melt becomes too rigid to permit of molecular orientation. The result is the amorphous, or colloidal, mass we call glass. In quickly chilled glass (*i.e.*, Prince Rupert bubbles), the internal strains are so great that the glass is actually explosive; and in the ordinary process of manufacture, glass must be annealed to render it less brittle. This is accomplished by slowly cooling the glass, keeping it at a low heat for a long time so that there may be a partial adjustment of the aggregation tendencies of its particles. Gelatine jellies, and soft metals, like lead and tin, act similarly, but because of their softness anneal spontaneously at room temperature.

If the composition or heat treatment of the glass is such that crystallization occurs—the phenomenon is termed devitrification—the glass becomes cloudy or opaque. The inherent tendency toward crystallization exists even in clear glasses, and may be realized after a long lapse of time. Thus ancient Egyptian and Roman glasses are frequently found to be devitrified. But though old leaden roofs consist of metal showing coarse crystals, ancient iron shows practically the same structure as modern iron. Iron consists mainly of the crystalline phase, which is stable, not of the colloidal phase which is metastable and can undergo slow hysteresis; besides, iron does not undergo annealing at ordinary temperatures.

[3] For results of ultramicroscopic examination of quickly and slowly chilled soaps, see J. Alexander: *Trans.* (1919) **60**, 466; *Jnl.* Soc. Chem. Ind. (1909); *Trans.* Am. Inst. Chem. Eng. (1909) **2**, 210–228.

[4] *Zeit. f. Elektrochem.* (1904) **10**, 532.

Process of Crystallization

The effects of the mechanical and heat treatment of metals may be studied by observing what happens on the slow cooling of a hot saturated solution of a crystalloid salt, sodium chloride, for example, since it has no water of crystallization. As the kinetic energy of the system drops and the capacity of the water to maintain the salt molecules (or their ions) in motion diminishes, some salt molecules are, as it were, extruded from the solution, only to be dissolved again while others are extruded; for there exists a condition, not of static, but of kinetic equilibrium, varying with the temperature.

If, however, a number of salt molecules are extruded in such a position and so close to one another that they may cohere, there is formed a crystal nucleus, or "crystallogen," that will tend to take from the cooling solution more extruded molecules than it gives back. Such dominant nuclei tend to form on the relatively cooler walls of the containing vessel, or on any added nucleus or foreign surface. Quick cooling produces more extruded molecules per unit of time, and agitation tends to bring the extruded molecules into contact; therefore both these factors tend toward the formation of more numerous and smaller crystals. Where large crystals are desired, it is the practice to crystallize in large tanks, which are carefully insulated and left undisturbed for weeks.

Extreme care is necessary to grow large perfect crystals and the temperature must be controlled within very narrow limits. R. W. Moore[5] has grown clear, perfectly developed crystals of Rochelle salt 3 in. long in a thermostat sensitive to about 0.01°. He found that crystals grow faster near the bottom of the crystallizing vessel than at the top, which is evidence of a gravitational accumulation of molecular groups at the bottom quite analogous to the separation of the particles in colloidal solutions, as demonstrated by Perrin.

Crystallization continues until the kinetic equilibrium corresponding to the final temperature is reached and the discrete crystals of sodium chloride bathed in a mother liquor containing a residual amount of salt in solution or true crystalloid dispersion are obtained. Impurities tend to collect in the mother liquor; if they are protectors (in the colloidal sense) they may inhibit or modify crystallization as they accumulate.

Crystallization of Metals

Even with pure metals under the best conditions, the path of crystallization is not as smooth as in the case of salt solutions. It has many complicating factors. There is no foreign restraining solvent, the vis-

[5] *Jnl.* Am. Chem. Soc. (1919) **41**, 1060.

cosity is great, the attraction between the closely packed metal molecules is tremendous, and the metal soon forms a hard skin so that the interior crystals are formed under pressure or strain. With some metals there may be formed a geode-like center, where slower cooling and lessened or more equalized strain may result in the formation of large well-developed crystals.

But the metal seldom reaches the crystallization equilibrium for the enormous increase in viscosity that accompanies its rapid loss of heat prevents the aggregation tendencies of the metal molecules from entirely establishing themselves, and there results a mass of metallic crystals embedded in a finely dispersed solid metallic "mother liquor," the so-called amorphous phase.

The amorphous phase is colloidal, as its name, appearance, and properties indicate, and contains a mixture of submicroscopic crystals or crystal fragments with unoriented or random clusters, possibly in the form of isotropic golbulites. The globulitic form, according to many investigators, seems to be a precursor of the crystalline condition. At higher temperatures, before visible crystallization occurs, the whole metal probably exists as an isocolloid. The extent to which this state is altered in the direction of a visibly crystalline mass, embedded in a colloidal matrix, depends largely on the speed of chilling. In impure metals and in alloys, the composition of the phases and the presence of substances that hasten or inhibit crystallization are important factors.

Von Weimarn holds the view, in which the writer does not concur, that all molecules and molecular groups are crystalline, that crystallinity is the only internal state of matter, and that in general no amorphous substances exist in nature. This view would give to the words amorphous and crystalline significations they do not at present possess. Besides, the X-ray spectroscope shows[6] that many organic colloids (gelatine, starch etc.) and also some inorganic colloids (silicic acid and stannic hydrosols) consist of, or contain, groups of molecules arranged in an unoriented, haphazard, or random manner; so that even if the molecules themselves are crystal prototypes, they can and do occur in non-crystalline groups.

Zay Jeffries[7] has shown that with metals, in general, the cohesion of the amorphous phase equals that of the crystalline phase at the lowest recrystallization temperature, which he terms therefore the equicohesive temperature; based on this he has explained the mechanical behavior of metals at various temperatures. At higher temperatures than the equicohesive point, the cohesion of the amorphous phase decreases more rapidly than that of the crystalline phase, *i.e.*, it becomes relatively softer;

[6] Scherrer; Nachr. Ges. Wiss. Göttingen (1918) C. A. **13**, 2624.

[7] *Trans.* (1919) **60**, 474; *Jnl.* Am. Inst. Metals (1917) **11**, 300–324; *Jnl.* Inst. Metals (1918) **20**, 109–140.

whereas at lower temperatures the cohesion is greater and increases with much greater rapidity than that of the crystalline phase.

These differences between the two phases are intelligible from the following considerations: The atoms in the crystalline phase, although arranged in regular layers, are on the average more closely packed and therefore at lower temperatures cannot draw together as much as those of the amorphous phase, which consequently becomes relatively stronger at lower temperatures. At higher temperatures, the molecules of the amorphous phase become separated and mobile more readily than those of the crystalline, for they possess initially more potential energy since they are less closely packed and are, therefore, less strongly held to one another by molecular forces. The fact that, even at room temperatures, some of the molecules of some metals possess mobility was demonstrated by Roberts-Austen, who showed that gold and lead placed in contact for several years slowly diffused into each other.

As a result of this preferential softening, the amorphous phase, at relatively higher temperatures, acts like a viscous solvent surrounding and nourishing the more rigid crystals; and as increasing temperature renders this solvent less viscous, the metal strives toward crystallinity, which represents the position of minimum mechanical potential. Some metals, like lead, undergo such molecular readjustment, even at room temperatures. During this process of recrystallizaton below the melting point, in general, large crystals tend to grow at the expense of the small ones. Therefore the smaller metal crystals would preferentially dissolve in the amorphous phase. Bearing in mind that the growth of a crystal means that there are deposited upon it more molecules or molecular groups than are dissolved off, the larger masses would naturally get most of these extruded units just as happens in the cosmic field. The larger crystals have the advantage of exposing to the solvent action of the amorphous or colloidal phase less surface per unit of mass; and when metal molecules or molecular groups deposit on a crystal, the heat of crystallization helps to make the amorphous phase more fluid.

Do the small crystals dissolve molecule by molecule, or in molecular masses as well? It would seem that in some cases at least molecular groups are dissolved off and transported, for in strained metals especially recrystallization is extremely rapid. Thus when sheet aluminium[8] is heated to a suitable temperature recrystallization takes place like a flash and the originally smooth sheet suddenly becomes coarsely granular. The writer has observed[9] ultramicroscopic particles streaming from a crystal of sodium citrate as it went into solution, indicating that initially solution took place, at least partly, in colloidal molecular masses.

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[8] G. H. Gulliver: *Jnl.* Inst. Metals (1918) **20**, 158.

[9] Alexander and Bullowa; "Archives of Pediatrics." 1910.

The amorphous phase becomes, therefore, a medium for the transfer of atoms, molecules, or molecular groups from the smaller to the larger crystals, and also tends to annihilate itself by allowing its constituent oriented and unoriented particles to be incorporated into the larger crystals.

The preceding statements apply only to pure metals, which are practically never used, for most commercially pure metals contain impurities; besides, most metals are used in the form of mixtures or alloys. The introduction of a single impurity, even in minute quantities, usually produces a marked change in the properties or behavior of the metal (*i.e.*, 1 part of carbon in 10,000 parts of iron, or 1 of copper in 10,000 parts of gold). As in many cases this effect involves, at some stage, the direction, modification, or inhibition of the normal crystallization of the metal by a colloidal dispersion of some substance or substances, the effect of colloids upon crystallization must be considered.[10] Most of the experiments in this field have been made with aqueous solutions or dispersions, and the rule seems to be that a colloid which is absorbed by, or which forms an adsorption compound with, the initial colloidal aggregations of the crystallizing substance either prevents the growth of its crystals or groups beyond colloidal dimensions, or forces their growth to assume globulitic or dentritic forms that vary with each substance, colloid, and set of conditions. Thus gelatine, gum arabic, and similar stabilizing or protective colloids, even in small quantity[11] oppose the aggregation of the gold atoms at the instant of their liberation to such an extent as to yield a highly dispersed red hydrosol under conditions that would otherwise yield a coarse blue or black gold suspension.

This resemblance led me to comment as follows regarding metals:[12] "Now while the question is one of very great complexity, many of the facts at present available seem to indicate that one of the causes favoring the fine-grained structure is the inhibition of crystallization by substances colloidally dissolved in the molten mass."

The presence in a metal of a second metallic or non-metallic element, whether as an intentional addition or as an accidental impurity, opens a wide range of possibilities, which may be roughly outlined as follows:

1. The second element may form a definite compound with the metal, or it may not.

2. If formed, the chemical compound may be stable at all temperatures or only within a certain temperature range; or there may exist a reversible equilibrium, with a lag on either side of the equilibrium point.

[10] See J. Alexander: *Koll. Zeit.* (1909); *Jnl.* Soc. Chem. Ind. (1909). Another paper is in preparation.

[11] Excessively minute quantites may have the contrary effect and actually sensitize. While this condition has not been observed in metals, it possibly forms the basis of the phenomena known to physicians as anaphylaxis.

[12] *Jnl.* Soc. Chem. Ind. (1909).

3. The second element or its compound with the metal may be soluble in or miscible with the metal in all proportions; or, as is usually the case, there may exist zones of thermal or percentage solubility, dispersion or peptization; or even practical nonmiscibility at all temperatures, in which case there is usually a certain degree of segregation.

4. Dissolved or dispersed elements or compounds may materially alter the melting point, viscosity (internal friction), surface tension, vapor pressure, freezing point, conductivity, allotropic equilibrium, and crystallization tendencies of the metal.

The presence of still other elements complicates the situation and when to these variable factors we add effects of mechanical treatment and the thermal history of the section of metal under consideration (which involves such factors as speed of chilling, size and shape of the original mass, hot and cold working, tempering), the impossibility of framing one general law that will cover the behavior of impure metals and alloys is apparent. Each case must be considered by itself.

Tin-lead Alloys

All the tin (melting point 232°)-lead (melting point 327°) alloys melt at a lower temperature than the melting point of lead. The alloy containing 63 per cent. tin and 37 per cent. lead has the lowest melting point. If the metals are mixed in other than eutectic proportion, on cooling, the excess metal tends to crystallize out alone leaving fluid the largest possible amount of eutectic, which solidifies later. That the eutectic does not consist of a chemical compound is brought out by a microscopic investigation; it is usually laminated and can be brought into relatively coarse dispersion by slow cooling.

But some forces do control the formation of the eutectic. As the fused alloy approaches solidification, the lead, having the higher melting point, begins to form molecular groups, crystallogens, or tiny crystals. This aggregation of lead molecules is opposed by the more fluid tin, thus lowering the freezing point of the mixture. Diminishing thermal agitation allows the tin to form groups and a stage is reached where both metals exist largely in the colloidal state.[13] In this zone a colloidal adsorption compound is formed, the ratio 63 tin to 37 lead being consequent upon their specific forces; any excess of tin or lead is free to crystallize independently. In the eutectic, the adsorbed lead interferes with the rapid crystallization of tin to such an extent that, if quickly cooled, its structure is extremely fine. As with all colloids, this represents a metastable condition, and if the temperature is kept within limits which permit

[13] All pure metals in solidifying pass through an isocolloidal zone, the narrowness of which is indicated by the sharp peak or cusp in the inverse-rate curve. For curves see W. Rosenhain: "Introduction to Physical Metallurgy," 85–87. N. Y., 1914. D. Van Nostrand.

molecular orientation without disruptive thermal agitation, the eutectic undergoes a gradual syneresis analogous to coagulation or demulsification—a further separation into its constituent phases. The laminated structure, common in eutectics, already represents the aggregation of the pre-existing colloidal dispersion, as will be especially pointed out later in the discussion of pearlite in steel.

Speaking of the tin-lead eutectic, Rosenhain[14] says that "this laminated character though often beautifully marked is not to be regarded as an essential feature of these substances. If a specimen of a well-laminated eutectic is heated for a long time at a temperature a few degrees below its melting point, the structure gradually changes, various laminæ coalescing to form lumps or globules, and the result is a much coarser granular structure. Such a granular structure may also be obtained if the molten eutectic is very slowly cooled.

"The eutectic alloy is the result, so far as its structure is concerned, of the simultaneous crystallization or freezing of the two component metals. As a rule one of these metals acts as the 'predominant partner,' and its own crystalline form determines the way in which the whole structure is arranged. It has shown that eutectic alloys, like pure metals, consist of an aggregate of juxtaposed crystals. These crystals are, however, merely skeletons formed of one of the metals with the interstices filled in by the other metal. In the case of the lead-tin alloys, the tin is the predominant metal, and each of the crystals of the eutectic is in reality a radiating structure, known as a spherulite, of tin carrying the lead in its interstices." This is clearly a picture of tin crystallized in the presence of adsorbed lead. Although tin has a lower melting point than lead, its superior crystallization power and speed make it predominant.

Rosenhain also points out[15] that lead-tin alloys containing up to about 16 per cent. of tin form a series of solid solutions, which approach their true equilibrium condition very slowly; he found that heating at a temperature of 175° for six weeks was required in order to bring the alloys approximately into their final state. This is indicative of the slowness with which the tin in these alloys is dispersed by the lead. Another observation is that alloys containing from 16 to 23 per cent. of tin exhibit an evolution of heat on cooling and a corresponding absorption of heat on heating at 149°. Rosenhain's explanation is that this is due to the diminution at that temperature of the capacity of lead to dissolve tin. In any event there is some form of non-stochiometric molecular aggregation, accompanied by an evolution of heat, quite analogous to what happens when silver hydrosols coagulate. Thus J. A. Prange found[16] that

[14] *Loc. cit.*, 133.

[15] *Loc. cit.*, 132; also Rosenhain and Tucker: *Phil. Trans.* Roy. Soc. (1908) **209A**, 89.

[16] *Recueil des. Trav. Chim. des Pays Bas* (1890) **9**, 121–133.

upon precipitation by ammonium citrate, 1 gm. of colloidal silver developed from 250.98 to 126.73 calories, depending on the concentration of the solution; and the further aggregation of the precipitate by sulfuric acid set free an additional 60 calories. But here restraining water films were present, and the final product was not a solid metal.

Another point of interest in the lead-tin alloys is found in the solder used by plumbers. At about 210°, this alloy begins to extrude crystals of lead into the fluid eutectic cement, rendering it pasty and easy to mold into the desired shape. Here the eutectic acts as a viscous colloid or glue thickened by the addition of clay or other fine insoluble filler.

The introduction of the highly crystalline antimony (melting point 630°) into the lead-tin alloys results in the early formation of crystals of antimony or of the hard brittle compound Sn-Sb, with the result that the ternary alloy is much harder. Type metal, which varies in composition according to price and service conditions, is usually chilled quickly, which is conducive to hardness and fine structure. White bearing metals, on the other hand, are usually cast in larger masses and chill more slowly; and their composition is chosen to yield hard wear-resisting crystals of Sn-Sb embedded in a colloidal plastic eutectic, which can adapt itself to the bearing's irregularities of shape and pressure.

Brass

Brasses containing less than 30 per cent. of zinc, whether quickly or slowly chilled, always consist of a solid solution of zinc in copper known as the pure α brass.[17]

The α brass is really an adsorption compound between copper and zinc, in which the large percentage of copper with the high melting point of 1083° aggregates so rapidly that even in so-called quickly cooled specimens, the zinc (melting point 419°) is for the most part so finely dispersed as to be only partly adsorbed by the copper; hence the dendritic structure which shows a copper crystallization as modified by adsorbed zinc, the amount of which increases from the center outward as the copper aggregates and the mother liquor becomes richer in zinc. It is probable that small pieces of α brass drastically quenched from fusion in liquid air would appear homogeneous in the microscope. As Rosenhain points out, the percentage of each metal and its state of aggregation are varying momentarily during cooling, and because of the wide disparity between the melting points of the two metals, homogeneity is favored either by extremely rapid quenching from fusion or by slow cooling or annealing, which favor more complete dispersion and adsorption of the segregated zinc.

[17] Rosenhain: *loc. cit.*, 142.

With brasses containing 30–37 per cent. of zinc, there appears a new hard, brittle, metastable phase β brass. Such brasses if quickly cooled are relatively hard and brittle, but if cooled slowly the β phase disappears. With more than 37 per cent. of zinc, the β phase is stable at all temperatures down to 470°, and the slowly cooled alloys possess the duplex structure seen in ordinary Muntz metal (approximately 40 per cent. of zinc). Carpenter holds that below 470°, the β phase decomposes into α and γ phases; in fact, that the β phase is an almost ultramicroscopic mixture of α and γ phases.[18]

Speaking of the γ phase of brass, Rosenhain says[19] that it "is exceedingly hard and brittle and its presence in the alloys renders them useless for any purpose where strength and toughness are required. This is a typical example of a law very widely applicable to alloys, viz., that those phases of a binary system which contain the two elements in anything like equal proportions are hard and brittle, only the alloys near the ends of a series being as a rule sufficiently strong and ductile to be of practical utility. We have already seen that the β phase is harder and more brittle than the α, so much so that the best brasses, in which strength and ductility are of importance, are generally made with a zinc content of approximately 30 per cent., this being the cheapest alloy which does not contain the β phase."

Von Weimarn[20] has shown that with solutions medium concentrations are favorable to the development of relatively large crystals, whereas dilute solutions tend to yield colloidal dispersions; this seems to hold true also in mixtures of two metals. The amorphous phase of most metals is stronger at ordinary temperatures; and highly crystalline metal, deficient in the amorphous phase, is brittle because it tends to split along the lines of crystal cleavage. We should therefore expect brittleness where the component metals of a binary alloy are in about equal proportions, for this concentration works against the development of colloidal metal and in favor of larger and more perfect crystals.

Iron and Steel

Since the behavior of the iron-carbon alloys is greatly influenced by the allotropic changes of iron, these should be considered first. After freezing at about 1505°, upon further cooling, pure iron shows a large evolution of heat at about 900°, known as the thermal arrest point Ar_3, and a smaller evolution of heat at about 780°, known as the thermal arrest point Ar_2. It is generally accepted as a fact that above 900° the iron exists in the γ form, which is non-magnetic, and below 780° in another allotropic form α iron, which is magnetic and exhibits a different crystal-

[18] This means colloidal dispersion, favorable to hardness.

[19] *Loc. cit.*, 145.

[20] *Koll. Zeit.* (1908) **3**, 282; (1909) **4**, 27.

lization from γ iron. Rosenhain believes[21] that the weight of evidence shows that between 900° and 780° the iron exists in a third allotropic form, known as β iron, which has the same crystal form as α iron but resembles γ iron in being non-magnetic. Benedicks,[22] on the other hand, believes that the evolution of heat at 780° indicates not a transformation of a β allotrope into α iron, but the final disappearance of persistent γ iron molecules from the metal.

The apparently conflicting views can be reconciled by regarding the iron between these temperatures (900° and 780°) as an allocolloid or allodispersoid, the so-called β iron being an α-γ adsorption compound (α iron dispersed in γ iron), whose breaking up into the more completely oriented α iron sets free the relatively smaller amount of heat at the point Ar_2. This view accounts for the following facts: (1) β iron has the same crystal form as its "predominant partner" α iron, but is not magnetic; magnetism seems to depend on a peculiar regular molecular orientation;[23] (2) γ iron dissolves iron carbide whereas β iron and α iron do not; whatever γ iron exists in the β zone is adsorbed by or in some kind of loose combination with the dominant α iron and is not free to exert its solvent power on iron carbide; (3) the increase in strength when α iron is transformed into β iron, the formation of some γ iron by increasing temperature over about 780° results in the formation of the α-γ adsorption compound, which increases the free surface and strength of the system; (4) the fine acicular structure of β iron is indicative of crystallization in the presence of a colloid.

A low-carbon steel, containing say 0.2 per cent. carbon, which dissolves in the liquid iron as Fe_3C, when freezing down to 840° consists of an apparently homogeneous solid solution, or dispersion of iron carbide or cementite in γ iron. At 840°, the α-γ dispersion (β iron) forms (Ar_3); and at 750° the residual α-γ adsorption compound decomposes into α iron (Ar_2). The steel now consists of α iron crystals dispersed in a "solid solution" of iron carbide in γ iron. With further cooling, the quantity of α iron crystals increases until at a little below 700° the remaining γ iron-carbide solid solution is transformed into a eutectoid mixture of α iron (ferrite) and iron carbide (cementite), with an evolution of heat (Ar_1).

This last transformation seems to be the breaking up of an adsorption compound between γ iron and iron carbide, the former transforming into α iron and the latter being set free to form aggregations of its own. This adsorption compound is the cause of the carrying over of some of the γ iron through the so-called β iron zone to the eutectoid point, where,

[21] *Loc. cit.*, 170.

[22] *Jnl.* Iron and Steel Inst. (1912) **86**, 242.

[23] The so-called Haeussler alloys are magnetic although their constituents individually are not. According to A. W. Hull, *Phys. Rev.* (1919) **14**, 540, magnetism depends on the distance between atoms rather than on their arrangement.

with increasing carbon content, increasing quantities of heat are evolved. The allotropic transformation of the iron becomes practically negligible after the steel contains about 0.5 per cent. carbon (or about 7.5 per cent. Fe_3C). Steel of eutectoid composition (about 0.9 per cent. C equals about 13.5 per cent. Fe_3C) exhibits only a single thermal arrest point, at which it glows visibly. This phenomenon, known as recalescence, is indicative of a sudden large release of energy consequent upon the breaking down of the extensive metastable system γ iron-cementite: two delayed transformations occur simultaneously, the iron transforms from γ into α, and at the same time the released cementite aggregates. The inhibition of the allotropic iron transformation shows that, in eutectoid steel, the large percentage of Fe_3C has carried over practically all the γ iron in metastable condition to the eutectoid point. The presence of such elements as silicon and manganese will perceptibly change the location of the eutectoid point, illustrative of the easy disturbance of colloidal systems by foreign substances.

But whether this view is accepted, or whether the change is regarded as a separation of carbide from γ iron solid solution, it is evident that there is suddenly released from some kind of solution or combination, Fe_3C, an insoluble substance possessing considerable cohesion: this cohesion causes the Fe_3C to attempt to aggregate against the interference offered by the now highly viscous iron. This is an ideal condition for the development of a colloidal system; the cohesive power of the cementite, however, is so great that in unquenched steel it usually appears interspersed with α iron, or ferrite, as fine plates or fibrils, yielding the finely laminated structure known as pearlite because under proper illumination it exhibits the iridescent luster of mother of pearl. This iridescence is evidence of the fineness of the pearlitic structure, which like Pleurosigma, taxes the highest powers of the microscope for its successful resolution, the lamellæ being often less than 0.2 μ apart.

Microscopically, eutectoid steel (approximately 0.9 per cent. carbon), when slowly cooled, consists entirely of pearlite, thus corresponding to the pure eutectic of ordinary alloys.[24] But with very slowly cooled steel, or with steel reheated for a long time at about 900°, the cementite tends to form balls or globules, the liberated ferrite forming larger crystals at the same time.[25]

Quenched or quickly cooled steels, on the other hand, exhibit an entirely different set of microscopic pictures and mechanical properties from slowly cooled steel, which vary with the speed of chilling. Arranged in the order of their formation on progressive cooling, the following constituent forms of the iron carbide dispersion are recognized by metallurgists:

Austenite, white apparently structureless streaks of γ iron solid solution, when preserved as such down to ordinary temperatures either as the

[24] Rosenhain: *loc. cit.*, 175.

[25] Rosenhain: 278.

result of quenching or because a third alloying element inhibits its decomposition, *i.e.*, manganese in manganese steels.

Martensite, the first stage in the aggregation of the γ iron solid solution. This is the hardest constituent of hardened steels; it varies widely in its structural details but is mainly acicular.[26]

Troostite, a dark-etching constituent with characteristic rounded or woolly outlines, is found particularly in hypoeutectoid steels at the edges of martensite grains, especially where they border on ferrite. By a suitable rate of cooling, or by proper tempering, martensite can be entirely converted into troostite.[27] Benedicks[28] says: "After studying some of the colloid literature, it was entirely clear to me as far back as 1905 that the nature of troostite is simply explained; it is a solid colloidal solution of cementite in iron (a solid cementite ferrosol). In other words, troostite may be conceived of as a highly dispersed intermediate between martensite, the true solid solution, and pearlite, the coagulum. . . . Troostite is a pearlite in which the constituent particles are ultramicroscopically small." With steel containing 1 per cent. carbon, Benedicks obtained the following results, the test pieces being cylinders 50 mm. long by 6.5 mm. in diameter.

Temperature of Steel Degrees	Time of Cooling to 100°C Seconds	Result of Microscopic Examination
950	3.07	Only martensite
848	4.32	Only martensite
750	4.11	Only martensite
715	5.33	Martensite with traces of troostite
695	6.2	Martensite with traces of troostite
725	9.5	All troostite

The last specimen had been wound with 1-mm. iron wire so that its weight was increased from 12.3 to 27.5 gm., thus lengthening the cooling period. This shows that the speed of aggregation is so great that within a few seconds all the martensite may be transformed into troostite.

Sorbite.[29]—"When the rate of cooling is further lessened or the temperature of reheating or tempering is further increased, the steel is permitted to progress somewhat further toward the final state of ferrite plus cementite. Instead of the troostite described above, we find a constituent still devoid of any visible detailed structure under the highest available magnifications, but not etching to such a deep color as troostite and without the peculiar rounded outlines. This is often called "sorbite," but it may be regarded as simply a variety of pearlite in which the two constituents are so finely divided that they cannot be microscopically separated. The dividing line between pearlite and sorbite, indeed, is simply a question of microscopic resolving power."

[26] Rosenhain: 179.
[27] Rosenhain: 183.
[28] *Koll. Zeit.* (1910).
[29] Rosenhain: 183–184.

Pearlite has been dealt with.

TABLE 1.—*Constituent Forms of Iron-Iron Carbide Dispersion*

Iron-Cementite Dispersions	Nature of Dispersion	Crystal Structure
Austenite	Solid solution?	Structureless streaks.
Hardenite	Colloidal	Structureless martensite.
Martensite	Colloidal	Generally acicular but varies; it may be very fine.
Troostite	Coagulation begun	Rounded or woolly (globulitic).
Sorbite	Coagulum	Fine pearlite, not microscopically resolvable.
Pearlite	Coagulum	Laminated; may segregate into balls.

TABLE 2

Pure Iron	0.2 Per Cent. Steel	0.9 Per Cent. Steel
$900°$ Ar_3 — γ iron forms $\alpha - \gamma$ adsorption compound (β iron)	γ iron-cementite solid solution	
Largest thermal point	$840°$ Ar_3 — $\alpha - \gamma$ compound forms late because of cementite.	This is eutectoid steel. So much cementite is present that no $\alpha - \gamma$ adsorption compound is formed, the γ iron being held in metastable condition by the cementite, down to Ar_1.
Allocolloidal zone		
$780°$ Ar_2 — $\alpha - \gamma$ compound decomposes into α iron.		
	$750°$ Ar_2 — $\alpha - \gamma$ compound changes to α iron.	
	$700°$ Ar_1 — γ iron cementite adsorption compound decomposes, γ iron changes to α iron, and cementite is liberated and aggregates.	$700°$ Ar_1 — Sudden change of all the iron from γ to α, with liberation of all the cementite.

Granting that in austentite the cementite is in true molecular dispersion, which I consider doubtful especially after solidification has begun, it seems evident that, of the remaining members of the iron-cementite dispersion systems martensite and troostite are to be regarded as within or approaching the colloidal zone of dispersion, whereas sorbite and pearlite are coagula of the pre-existent colloidal systems, the latter visibly so. In the colloidal systems, cementite (Fe_3C) is the dispersed phase and iron the dispersing phase, as the pearlite coagulum consists of cementite interspersed in ferrite. In martensite, crystal formation is only incipient, being inhibited by the high viscosity of the dispersing medium and perhaps also by the adsorption of a small residual quantity of γ iron (consequent upon lag in its transformation), or of impurities. With troostite the globulitic stage is reached; it is found in crystallization inhibited by colloids, reminding one somewhat of the "clumping" of typhoid bacteria

in the Widal test. It must be remembered that metal surfaces etched by various reagents are artifacts, from which the original detail of the unetched metal must be inferred.[30]

Although theoretically there is no sharp line of demarcation between any of the members of the iron-cementite dispersion series, the sorbite-pearlite group shows the characteristics of coagulated colloids or gels, as opposed to the martensite-troostite group which represents higher dispersion, with troostite appreciably on the road to coagulation.

There is other distinct evidence of the colloidal nature of the cementite in hardened steel. Prof. H. C. H. Carpenter, speaking first of annealed or slowly cooled steel, says:[31] "This carbide can be separated from the steel by appropriate solvents which remove the iron. On the other hand, it is not possible to separate any carbide of iron from a properly quenched tool steel. When the latter is treated with dilute acids, the steel dissolves without residue and liberates a complicated mixture of hydrocarbons, both liquid and gaseous. There is, therefore, a fundamental difference in the form of the carbide in a quenched, as compared with an annealed steel. In the former it is wholly dissolved, in the latter wholly segregated." This last statement is too dogmatic, and he retrieves it saying: "When hardened steel is softened by annealing, the carbide of iron is gradually precipitated. If the annealing be carried out at low temperatures it is precipitated in the form of ultramicroscopic particles which are known as troostite. On raising the temperature, the troostite passes into another variety known as sorbite, and at still higher temperatures, well segregated pearlite results. The gradual tempering and softening of hardened steel is caused by the precipitation of iron carbide in these forms, together with the soft α iron, and as to this no difference of opinion exists."

The formation of hydrocarbons upon the solution of hardened steel in acid shows that the particles of Fe_3C are so small that upon their decomposition the nascent hydrogen is able to combine with the liberated carbon, which must appear in particles approximating molecular dimensions and within the range of molecular attraction. The variety of hydrocarbons formed is evidence of the great diversity in the size of the carbide groups, rather than of the existence of a number of different carbides, or chemical compounds; in other words, the carbide in properly hardened tool steel exists almost entirely in colloidal form. Great chemical activity is generally consequent upon colloidal dispersion. Raffo and Pieroni showed that, while fine precipitated sulfur does not affect cold silver salts and does so only partially upon boiling, colloidal sulfur reduces them energetically even at ordinary temperatures. Fine lead, produced by

[30] Bechhold: "Colloids in Biology and Medicine." Chap. 23. Trans. by J. G. M. Bullowa. D. Van Nostrand & Co. 1919.

[31] The Hardening of Steel. *Engineering* (Mch. 14, 1919) **107**, 386.

heating dry lead tartrate in a tube, takes fire instantly in the air, as does the phosphorus left upon the evaporation of the solvent from its CS_2 or ether solution.

Waiving the question as to whether the cementite in austenite is colloidal (and I think that at least as the steel freezes it becomes so), it seems that the very hard martensite is a colloidal dispersion of cementite in iron with "hardenite" as its higher dispersion, troostite its incipient globulitic aggregation product, and sorbite and pearlite its successive coagulation stages. This view will perhaps reconcile the "allotropic" and "amorphous" theories[32] that have been advanced to answer the question as to the constitution of martensite and the cause of its great hardness. Considering martensite as a cementite ferrosol, it is "amorphous" in the sense that its particles, even if actually crystalline, are mostly not microscopically resolvable; and, especially in low-carbon steels on quick chilling, there is a tendency to carry over into the solid state some of the α-γ allocolloid, so that the iron dispersing phase itself may represent a colloidal dispersion, consisting mainly of minute α iron particles. Because of the highly colloidal nature of the martensite and the consequent great development of free surface in it, it is extremely hard. Large percentages of oil colloidally dispersed or emulsified in water yield very firm stiff masses, although both phases are originally liquid.

The fact that austensite, though harder than pearlite, is not as hard as martensite, indicates that the latter represents a point, or rather a zone, of maximum degree of colloidality,[33] that is, there appears to be a certain degree of subdivision or dispersion, not necessarily the same with all substances, in which the dispersion system exhibits colloidal or surface phenomena to the highest extent, this effect declining not only with increasing aggregation or coagulation, but also with further peptization and the approach of true molecular dispersion or the formation of smaller molecules.

The behavior of hypoeutectoid steels (containing less than 0.9 per cent. carbon) is naturally complicated by the fact that the transformation of the excess γ iron (that in excess of the γ iron-cementite adsorption) into α iron, or the breaking up of the α-γ adsorption, takes time and exhibits a lag that is most marked in the quickly cooled specimens. On the other hand, with hypereutectoid steels (containing more than 0.9 per cent. carbon) the excess of cementite tends to crystallize out in slowly cooled specimens and to yield some undecomposed γ iron-cementite solid solution in quickly cooled specimens. McCance[34] showed that on adding carbon to iron, the hardness of the quenched steels increases up to 0.7 per cent. carbon and remains constant between this point and

[32] Rosenhain: 180–182.

[33] This is the subject of a separate paper, now in preparation.

[34] H. C. H. Carpenter, *loc. cit.*, 388.

1.18 per cent. This indicates a zone of maximum colloidal effect, which probably covers the zone of maximum degree of colloidality referred to. The addition of manganese to steel, as Maurer has shown, retards the aggregation of the cementite so that ordinary slow cooling yields martensite, probably because the viscosity of the dispersion medium (iron) is increased by the manganese (melting point 1225°) which by its surface or adsorptive action acts like a protector in opposing the aggregation of the martensite constituents. On the other hand, the manganese increases the speed of the transformation, when it does occur, because the manganese then exerts its force in the direction of the readjustment. Still larger percentages of manganese prevent any transformation at all, yielding austenite.

The amorphous theory advocated by Rosenhain[35] stresses particularly the entire absence of regular orientation or crystallization in the so-called amorphous phase, in which the molecules are supposed to be in the random and, mainly, isolated state assumed to exist in liquids. I believe, however, that the amorphous phase consists largely, if not entirely, of molecular groups, many of which may be oriented in the form of ultramicroscopic crystals or crystal fragments; and that its properties are due, not to the entire lack of orientation among its particles, but to the fact that many of its molecular groups are of colloidal dimensions. As in metals the molecules are very close together and possess extremely high cohesion or crystallization tendency, it does not seem possible that the amorphous phase can be composed entirely of isolated molecules or even entirely of non-crystalline groups. With gold hydrosols where the dispersing water exercises a restraining influence, the X-ray spectroscope shows that the ultramicroscopic, and even that the amicroscopic, gold particles are crystalline. With the most drastically chilled metal, allowing for the high viscosity and its rapid increase, it does not appear conceivable that no tiny ultramicroscopic crystals form, or at least that there is no grouping, regular or irregular, of the metal molecules. The facts are in harmony with the conception of amorphous metal as an isocolloid, that is as a dispersion of colloidal crystals, crystal fragments, or non-crystalline groups, forming a solid gel-like mass. The fineness of its particles, and the enormous development of free surface found in all colloids, are its critical factors.

The idea that metals, in the course of their aggregation, pass through a colloidal stage that exerts a powerful influence on their structure and properties, and may even be partly retained in the final product by protection, adsorption, crystallization, or increase in viscosity due to quenching, is not limited to the field of metallurgy; it may be applied to any substance or system where a portion or a component becomes colloidal

[35] *Loc. cit.*, 249.

while the remaining portion or components are outside of the colloidal zone. The case of glass has been mentioned, where some components apparently inhibit the ordinary crystallization of the others under operating conditions. This theory may also account for the fact that under one set of conditions Na_2CO_3 crystallizes with ten molecules of water, while under other conditions it may be crystallized with seven molecules of water; and the effloresced crystals hold only one molecule of water. Sodium sulfate acts similarly, forming Na_2SO_4, $10H_2O$ and Na_2SO_4, $7H_2O$ and the anhydrous salt Na_2SO_4.

Liquids appear to consist largely of atomic or molecular groups and solids of still more complex groups, the size and nature of which depend upon conditions;[36] and among these groups, those of colloidal dimension as a rule appear and must then be reckoned with. The twinning of crystals, which is a marked characteristic of γ iron, α brass, and especially of worked or strained metals on annealing, is probably due to colloidal influences. This and many other questions, such as the effect of other metals on iron and steel (so-called alloy steels) and the adsorption of gases at the free metallic interfaces, etc., though germane to this paper, must be left for future consideration.[37]

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[36] W. E. S. Turner ("Molecular Association," 99) says that "the formula of a substance shall be recognized as a function of the physical conditions under which it exists, so that the formula for elements is X_n, for compounds $(XY)_n$, where n is to be specified according to the conditions. Although we are far from realizing how n varies for most substances, the adoption of such formulas would bring home clearly the fact that both the physical and the chemical behavior of a substance may be closely dependent on the value of n."

[37] P. W. Bridgman found that while cylinders of soft tool steel (1.25 per cent. carbon) and soft chrome-nickel steel (Krupp Special E. F. 60.0) ruptured under the same pressures whether water or mercury was the pressure-carrying fluid in contact with the metal, when hardened the same steels broke at about one-third of the pressure with mercury as with water. The rupture was due to the amalgamation of the steel, which when once started spreads rapidly under the high hydrostatic pressure.

But even a pressure of 6500 atmospheres for 12 hr. failed to cause the amalgamation of hard or soft steel rods, although the rods were polished with fine emery paper immediately before being plunged into the mercury. On the other hand, hard and soft steels and cast iron (also aluminum, nickel, cobalt) were promptly amalgamated on the fresh surfaces formed by breaking the metals under mercury.

Bridgman says "dirt" prevents amalgamation; but from the recent work of W. B. Hardy, on fresh surfaces, and of I. Langmuir and others, on adsorption, it would seem that instantaneous adsorption from the atmosphere, probably of gases, is responsible, although a change in the nature of the surface may have some effect. Freshly cleaved sheets of mica show a similar effect; their initial coherence is speedily lost. With steel, as with gelatine jellies, the quickly chilled specimens show greater porosity because of the greater total efficient area of the diffusion paths consequent upon finer subdivision.

See The Action of Mercury on Steel at High Pressure, *Proc.* Am. Acad. Arts and Sci. (1911) **46**, 325–341; also subsequent papers.

DISCUSSION

PAUL D. MERICA,* Bayonne, N. J.—This paper emphasizes the fact that present methods of metallography have definite limitations. In a large number of cases the properties of metals and alloys may vary through quite remarkable ranges, without the possibility of following them by microscopic study. It is well known, for example, that the nickel-iron alloys may be obtained in magnetic and non-magnetic conditions, with no change in the structure that can be perceived by present methods. In a number of instances, such as duralumin, the mechanical properties may vary through a range of 100 per cent., based on the lower values, without any change in the structure of the material, so far as can be seen under the microscope. We are going to require other methods for the study of the structure of these metals; the most promising appears to be the X-ray spectrometer. Other methods, however, such as the study of the physical properties, electrical conductivity, thermal conductivity, and thermal expansion, may serve to give some indication of this structure.

Lead in a high brass may occur in several forms; in one there are no visible particles of lead but there is a mottled structure over the whole grain, which is generally ascribed to the presence of lead. I do not know whether there is any difference in the mechanical or other properties of the brass with the lead in these two conditions.

One other fact of interest is the statement, in paragraph 3 on page 8, "that one of the causes favoring the fine-grained structure is the inhibition of crystallization by substances colloidally dissolved in the molten mass." Aside from the possibility of obtaining fine-grained structures by the use of substances that may give a colloidal structure, an old practice of determining the carbon in the steel in the furnace was to quench a button and then examine the length of the grain, which is a rough indication of the rapidity of crystallization. It has been found that the higher the carbon, the longer the grain. Here is a case in which crystallization has been favored by the presence of an element that is atomically dissolved, whereas in cases where it is less highly dispersed, it may produce a finer grain.

E. E. THUM,† New York, N. Y.—Apparently the paper has been confined to a discussion of evidences of colloidal state in solid metal. The observations might well be extended to a consideration of metal in a liquid state; for instance, to certain phenomena that occur in the manufacture of alloy steels. We all remember, during war-times, the difficulties experienced in making high nickel steels with good transverse

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properties. Foreign metallurgists of note maintain that transverse weakness (or that combination of properties that shows up as flakes or woody structure in test specimens) is due to oxidized impurities in the metal and guard against these impurities largely by careful furnace practice. They have discovered that certain alloys are particularly susceptible to flakes and on the other hand certain alloying elements have an action on such melts similar to the clearing action of a small amount of electrolyte when introduced into a colloidal suspension. Under the microscope these solidified steels when they show slag inclusions of moderate size have properties in all directions which are normal; in the defective steels showing flakes and transverse weakness inclusions of that sort cannot be seen except with the greatest of care. Sometimes when defective steel is examined immediately after polishing, under the highest power microscope, without any etching, slag inclusion of most minute size can be seen. According to the definition of colloids given in this paper, these particles are not colloids, but correct furnace practice and a small amount of alloying element will flocculate these particles into the larger inclusions, and with this action will vanish the great danger due to transverse weakness.

Only recently metallographists have advanced the idea that some of the time-tested "phosphorus" reagents perhaps do not show phosphorus as much as they show extremely finely divided oxide; whether this oxide is in true solution, colloidal solution, or in minute extracolloidal particles in suspension, is a question. Under certain circumstances metal can hold oxide in most extraordinarily fine subdivision, almost in the form of a solid solution, and that kind is apparently the oxide which is so dangerous. It appears to be related closely to "ghost-lines" of microscopic size. An interesting speculation is whether the so-called deoxidizers, like spiegel or ferro-titanium, do not exert a most effective action by flocculation rather than chemical reaction.

One might think that questions regarding the nature of solidification and whether or not the metal solidifies with the large or small crystalline structure are more or less academic and of no value to the practical man, but the size of the primary crystallization has much to do with the amount of segregation occurring in the metal and also the ease with which the casting structure is broken by heat treatment. In other words, a metal which, as it solidifies, develops a closely packed aggregation of crystallization centers will not show such striking segregations of insoluble and partly soluble chemical constituents as will one that develops large grains. For the same reason subsequent heat treatments will much more easily break up the original structure and equalize by diffusion the soluble chemical constituents. In general, a fine grained ingot or casting is a much better metal to work with from a quality standpoint.

ZAY JEFFRIES,* Cleveland, Ohio (written discussion).—This paper cannot fail to stimulate thought in connection with atomic arrangement and its relation to physical and chemical properties of metals and alloys. The ideas put forth relate to the specific manner in which complexes are formed from constituent atoms. That numbers of atoms in a liquid metal should group themselves into more or less stable or unorganized groups varying in size, that is in numbers of atoms per group and in the manner of grouping of the atoms, seems quite probable.

The interpretation of the amorphous phase in metals as a colloid may meet with certain objections. For example, would a group of atoms so arranged as to form a colloidal particle in a good conductor like a metal carry a charge of electricity similar to a colloidal particle in an aqueous solution?

One of the most important points is that of a critical distribution of one constituent in another to produce maximum cohesion. The writer has suggested[38] a combination of amorphous and crystalline phases of a metal having higher cohesion than either phase singly, also that the martensitic state of steel strongly suggested a combination of two physically different constituents with higher cohesion than either one. Merica, Waltenberg, and Scott suggested a critical dispersion of $CuAl_2$ in aluminum, producing maximum hardness;[39] if the particles of $CuAl_2$ become larger or smaller than the critical size, softness results.

Mr. Alexander now proposes the idea of a critical dispersion as a general law. If this proves to be a general law, it will go far toward explaining the underlying reasons for the hardening of steel. This law, however, should be considered without exclusive reference to the colloid theory with a definite limit of the maximum size of colloidal particles. In other words, this law can be considered with respect to crystalline aggregates larger than $100\mu\mu$.

P. W. BRIDGMAN,† Cambridge, Mass. (written discussion).—Experiments made by the writer corroborate Mr. Alexander's theory that definite structures may exist in the liquid above the melting point. If water is compressed to about 90,000 lb. per sq. in. at a temperature below 0° C., it will be capable of crystallizing into two forms, which the writer has called ice V and ice VI. Ice VI is the unstable form, and ice V the stable, but ice VI almost always is formed on the first freezing, and it is difficult to induce the more stable ice V to appear. But after ice V has once formed, it almost always appears on subsequent freezing. This tendency

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[38] Effect of Temperature, Deformation and Grain Size on the Mechanical Properties of Metals. *Trans.* (1919) **60**, 474.

[39] Heat Treatment of Duralumin. *Bull.* 150 (June, 1919) 942.

† Jefferson Physical Laboratory.

persists even if the water is maintained in the liquid condition at some distance from the melting point for as much as 24 hr.

Mr. Alexander's opinion that the failure of iron to amalgamate under ordinary conditions may be due to an adsorbed layer of gas on the surface is the conclusion at which the writer arrived in an experiment mentioned on page 334 of the paper to which Mr. Alexander refers.[40] The experiment consisted in plunging into mercury a surface of broken iron in a small fraction of a second after the rupture. No amalgamation took place under these conditions. No ordinary "dirt" is sufficient to explain this effect, which is probably due to the rapid formation on the surface of a film of adsorbed oxygen. Computation by the kinetic theory of gases shows that, at atmospheric pressure, an exceedingly small fraction of a second is sufficient for the formation of a protecting film.

HENRI LE CHATELIER, Paris, France (written discussion*).—In the first page, Mr. Alexander defines with great exactness the expression "colloidal state." This state necessarily comprises two phases—subdivided material and the medium in which this material is dispersed. The properties of this state are inseparably connected with the dimension of the particles. This subdivision can bring about important modifications in the physical properties of the substance and can also affect the chemical properties.

I am not convinced of the accuracy of the conclusions that the author formulates on the subject of metals and metallic alloys. He takes no account of the surface tensions that always exist at the point of contact of two bodies. That is the key to the problem. These forces are usually considered too small to merit serious consideration. What must be considered is not the size of the force, but that of the energy stored up in the bodies. In other words, the surface energy is equal to the product of the tension by the surface of the body, and in colloids this surface is enormous, also the corresponding energy is much greater than is ordinarily supposed. A few figures will make this clear.

One particle of water weighing 18 gm. forms a sphere of 1.63 cm. radius, having an exterior surface of 33 sq. cm. Let us calculate what happens to this surface when the water is divided into smaller and smaller drops; for instance, drops having the radii of 0.001 millimeter, or 1μ, and 0.000001 millimeter, or 1$\mu\mu$, which are the limits between which colloids evolve.

Diameter of drops	1μ	1$\mu\mu$
Total surface of drops	2.04 sq. m.	2040 sq. m.

[40] *Proc.* Amer. Acad. (1914) **46**, 325–341.

* Translated from the French.

The second factor in surface energy is the surface tension.

Substance	States Existing Together	Temperature, Degrees	Surface Tension, Grams per Linear Centimeter
H_2	Liquid and gaseous	− 252	0.002
NH_3	Liquid and gaseous	− 29	0.041
H_2O	Liquid and gaseous	+ 20	0.076
Hg	Liquid and gaseous	+ 15	0.432
Pt	Liquid and gaseous	+1770	1.700
$SO_3.CaO$	Crystalline and solution	+ 15	1.120
$SO_3.BaO$	Crystalline and solution	+ 15	4.400

From the examples here given, it is apparent that metals have higher surface tensions than compounds of metalloids and that solid bodies in contact with liquids have still greater tensions.

The energy accumulated in one particle of water for different states of subdivision is:

Diameter of drops	1μ	1$\mu\mu$
Kilogram-meters	0.430	430
Calories kilog	0.001	1

That is to say, a particle of water divided into drops of 1$\mu\mu$, entering into chemical combination liberates 1 calorie more than the same weight of water taken as one compact mass. In the case of solid bodies in contact with liquids, and still more in the case of metals, the surface tensions, and consequently the corresponding energies, will be ten and one hundred times greater—equal to and often greater than the amounts of heat liberated in the most vigorous chemical reactions. As a result, the strength and tenacity are increased because these surface tensions are added to the internal cohesion of a homogeneous mass. The perimeter of the different grains taken together vary in inverse ratio with their dimensions. The resulting force for a surface tension of 1 gm. per linear centimeter is:

Dimensions	1μ	1$\mu\mu$
Total perimeter for 1 sq. mm	4 m.	4000 m.
Resulting tension	0.4 kilogs	400 kilogs

which is more than sufficient to explain the increase in strength of fine-grained alloys. It is doubtless true that the dimensions probably never are as small as 0.000001 millimeter, but in many alloys, notably pearlite, they go below 0.001 millimeter.

A second result of the fineness of solid bodies is the increase of the vapor tension and the solubility. Here, for example, are measurements of fine precipitates of calcium sulfate.

Dimensions of grains	2μ	0.3μ
Solubility per liter	2.08 gm.	2.56 gm.

These and similar measurements on barium sulfate were used as a basis for the calculations of surface tensions given above. In fact, thermodynamics gives exact mathematical formulas on the relation of solubility to this tension.

To this difference in solubility is due the increase in size of the particles in a precipitate obtained in chemical analysis by leaving the precipitate in the solution for an extended period, and which is used to facilitate the filtration of precipitates. The same phenomenon explains the increase in size of the grains in an alloy under prolonged heating. In fact, there seems to be no doubt that the colloidal state must have an effect upon the chemical properties as it has on the solubility. Cementite offers an apt example. In large crystals, that is to say, about 0.01 millimeter thick, it is easily attacked by a boiling alkaline solution of sodium picrate, which colors it a dark brown. On the contrary, the grains of pearlite are never colored by this reagent, except the exceptionally large grains seen in overheated steels that have been cooled very slowly. The colloidal cementite of troostite is not colored. Further investigation would no doubt disclose other analogous examples; but more often the colloidal substance will be more easily attacked, as it is the more easily soluble.

The theory of amorphous metals does not seem to me to have any necessary connection with the colloidal state. Moreover, the existence of this amorphous state is merely a hypothesis that has not been definitely verified. One can express whatever opinions one chooses on this subject, because they are not susceptible to experimental corroboration.

CARL BENEDICKS, Stockholm, Sweden (written discussion).—As stated by the author, the present writer, in 1905,[41] drew attention to the fact that the highly dispersed state of matter has considerable influence on the properties of alloys, especially in forwarding the rational explanation of the nature of troostite—concerning which about a dozen theories existed—as being a solid cementite ferrosol. This view explained the sharp solubility maximum found by Heyn.[42] A. Lottermoser,[43] then drew attention to the close analogy between the properties of gold ruby glass and troostite. Finally, Wo. Ostwald[44] gave a review of the facts known up to that time.

It is mentioned that for the Cu-Zn alloys Carpenter holds, "that below 470°, the β phase decomposes into α and γ phases; in fact, that the β phase is an almost ultramicroscopic mixture of α and γ phases." It is of considerable interest also to know that Carpenter[45] has found that this

[41] *Zeit. phys. Chem.* (1905) **52**, 733; *Jnl.* Iron and Steel Inst. (2, 1905) 352.
[42] C. Benedicks: *Jnl.* Iron and Steel Inst. (2, 1908) 217.
[43] A. Lottermoser: *Koll. Zeit.* (1911) **8**, 95.
[44] Wo. Ostwald: Kolloidchemie und Metallurgie. *Koll. Zeit.* (1916) **19**, 46.
[45] *Jnl.* Inst. Metals (1912) **8**, 51.

generally very stable β colloid is coagulated into coarse segregations of α and γ on the nucleus action of a vanadium alloy; this, so far as I am aware, has the interest of being the only solid analogon known in metallography of the coagulating influence of additions, well known in liquid systems.

When the Pb-Sn alloys are discussed no experimental fact is given, which proves that a colloid state makes itself perceptible. The curves alluded to in the footnote on p. 532 certainly do not prove more than that if an isocolloid zone exists, it must be very narrow; its existence, or consequences, is scarcely supported by any facts given.

It is to be regretted that scarcely any new experimental facts are adduced for the importance of the colloid state for metallography. The list, however, can easily be completed. Thus, the Fe-Ni alloys were earlier almost universally considered to be homogeneous solid solutions. The writer discovered[46] that on slow cooling these supposed homogeneous solutions are divided into two structural elements—those of the meteoric irons—which generally are of a submicroscopic size, constituting a colloid system. Indications of colloid constituents also occur in the Cu-Sn alloys, according to the description of Carpenter. Further, it was found[47] that on electrolysis from acetate solution a copper is obtained which must be considered to contain acetate in solid solution—as proved especially by the very high electrical resistance; between this solid solution and the segregated state, a colloidal intermediate state is highly probable.

Colloid enthusiasts are apt to claim most phenomena in nature to be of a colloid character. It is important not to go too far in this direction; it only will discredit this domain of knowledge. The author, on p. 531, mentions the phenomenally great influence produced, say by 0.01 per cent. of an impurity on the properties of a metal, and adds that in many cases this effect involves a colloidal dispersion. The difficulty in explaining the great increase of the hardness or electrical resistance of iron, introduced by a small fraction of an impurity, becomes very much greater if we admit the action to be of a colloidal character: the only possibility in such cases is to admit a true atomic dispersion; *i.e.*, a true solid solution. A system where cementite is in a colloidal state (troostite) is much less hard than when there is a solid solution (martensite); it cannot be correct to admit also the martensite to be a colloidal dispersion (as is indicated on p. 539); a nearer discussion shows that austenite and martensite must be considered as solid solutions, the first in gamma, the latter in alpha iron. The statement in the footnote on p. 535 "this means colloidal dispersion, favorable to hardness" can be quite true when compari-

[46] C. Benedicks: Feste kolloide Systeme in der Metallographie. *Koll. Zeit.* (1910) 7, 290.

[47] C. Benedicks: *Metallurgie*, 1907, 4, 5, 33.

son is made with the coagulum, but it is not true when the hardness is compared with that of the true solution.

JEROME ALEXANDER (author's reply to discussion).—The discussion has adduced many additional instances of the application of the principles outlined. It has also shown other aspects of these principles and has referred to some points that were perforce omitted in condensing the paper. Some of the questions thus omitted may be epitomized as follows:

1. Dynamic allotropy, especially of molten sulfur.[48] Here ammonia accelerates the attainment of equilibrium between the allotropes, whereas sulfur dioxide so retards it that chilling easily maintains the status quo.

2. Von Weimarn's work on transparent elastic sulfur[49] produced by chilling in liquid air sulfur heated to 400° C.

3. Bridgman's work on various forms of phosphorus, including a new black form that differs from the yellow and the red in being a conductor of electricity; this metallic quality is conferred by extremely high pressures.[50] (About 11,000 kg. per sq. cm.)

4. Wo. Ostwald's table showing eight isocolloids of water.[51]

5. Zsigmondy's work on gold ruby glass, which follows ultramicroscopically the aggregation of metallic gold through the colloidal zone.[52]

6. Bowen's work on the devitrification of glass.[53]

7. Bellamy's work on gold ruby glass, which confirms the view that stannic oxide exerts in glass the same protective or peptizing action on colloidal gold that it does in aqueous dispersion, *e.g.*, in the purple of Cassius.

8. General discussion of crystallization and a statement of some experiments showing the effect of colloids on crystallization.

9. Effect of colloids on the crystallization of plaster of Paris.[54]

10. Resemblance of photomicrographs of fine martensite to the dark field pictures of coagulated ultramicrons, *i.e.*, of casein.

11. Experiments showing some results of progressive subdivision with lead shot; the size known as "dust" clumps together when wet, whereas larger shot does not.

12. Production of dendrites of Pb and Fe by deposition of the metal in the presence of a colloidal protector, those of Fe recalling the acicular structure of martensite.

The chemist and physicist, in exploring the dark region of the atom, have revealed a world of subatomic phenomena; we are also learning

[48] W. E. S. Turner: "Molecular Association," 92. 1915.
[49] *Koll. Zeit.* (1910) **6**, 250.
[50] *Jnl.* Am. Chem. Soc. (1914) **36**, 1544–63.
[51] "Handbook of Colloid Chemistry," M. W. Fischer's translation, 1918.
[52] "Colloids and the Ultramicroscope," Alexander's translation, 1909.
[53] *Jnl.* Am. Ceram. Soc. (1919) **2**, 261–81.
[54] *Jnl.* Soc. Chem. Ind. (1909) **28**, 280.

much by investigating the colloidal zone lying between what are ordinarily termed physical and chemical. The metallurgist cannot omit consideration of submicroscopic or ultramicroscopic phenomena which, though hidden, are none the less real. I have asked those having proper facilities to examine with the X-ray spectrometer specimens of metals and alloys slowly cooled, and others drastically quenched. With mercury and low melting point alloys, like Wood's metal, it should be possible with this new instrument to follow molecular aggregation in metals under gradually decreasing thermal agitation.

Doctor Merica emphasizes the necessity of reckoning with colloidal phenomena. His observations on substances that favor crystallization are further reinforced by Bowen's work, for in glass Cl and SO_3 act as "mineralizers," showing the opposite to protective action.

I agree with Mr. Thum that we should seek information regarding the colloidal state in fluid metal, where it undoubtedly exists, for even if transitory it is of potent influence. The trouble-making inclusions in nickel steel of which he speaks are, partly at least, above colloidal size; but there is no sharp limit to the colloidal zone and particles much above the usual superior colloidal limit (100 $\mu\mu$) show effects consequent on their fineness of subdivision. The facts mentioned show that some substances in fine dispersion produce a weaker steel than the same material aggregated into coarser inclusions, just as one large hole may produce less weakness in a metal bar than a multitude of adjacent small holes having the same total area as the large hole.

The work of Merica, Waltenberg and Scott, cited by Doctor Jeffries, is an illustration of a zone of maximum colloidality, the hardness of the Cu-Al alloy diminishing on either side of a certain optimum degree of dispersion. As Doctor Jeffries suggests, the consequences of subdivision are not hemmed in by any arbitrary limits. Wells[55] suggests four general groups of degree of subdivision: (1) molar, including ordinary physical and even astronomical masses; (2) molecular, covering the colloidal zone and including much of what is called physical chemistry; (3) atomic, covering ordinary chemical changes; (4) electronic, covering subatomic phenomena. While quantum relations seem to predominate in (3) and (4), (2) blends insensibly into (1) and (3).

Professor Bridgman's remarkable work on the effect of high pressures merits the careful consideration of metallurgists, even his experiments with non-metallic substances, *e.g.*, phosphorus and egg albumin, the latter of which is coagulated by mere pressure. The powerful adsorption at fresh, clean, metallic surfaces is parallelled by freshly cleaved sheets of mica, which adhere if instantly put together but fail to do so after a brief exposure to the air.

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[55] *Jnl.* Wash. Acad. Sci. (1919) 361.

Professor Le Chatelier suggests that the surface tensions existing at phase interfaces are the key to the colloidal problem, and that I take no account of them. Surface tension is a resultant of what I term, in my paper, molecular or crystallization forces.[56] I have considered the forces without, however, discussing their origin, which would lead to theoretical discussion—residual valences, stray fields of force, etc. I thank Professor Le Chatelier for bringing forward details to support the view, which I expressed in my preliminary paper,[57] that with particles of colloidal size "such phenomena as surface tension and adsorption, which depend on the development of free surface, become enormously magnified. . . . The tiny force with which a drop of rain clings to the window pane becomes a factor to be reckoned with if the surface is increased millions of times."

Metallurgists will hardly agree that the existence of the amorphous state is a mere hypothesis. What they call amorphous metal is either colloidally or molecularly dispersed. Rosenhain believes that amorphous metal represents molecular dispersion, whereas I believe that the evidence indicates colloidal aggregation.

Professor Benedicks brings out many facts of interest. I thoroughly agree as to the danger of attributing everything to colloids, a danger I have often emphasized.[58] On the other hand the colloidal condition is ubiquitous and cannot be omitted from consideration, especially as in many cases it is a controlling factor. Professor Benedicks believes that troostite represents the inferior limit of colloidal dispersion of cementite, martensite being a solid solution. I believe, however, that martensite and hardenite represent colloidal dispersion of cementite, and so probably does austenite, as solidification is approached. Maximum hardness, covering martensite and hardenite, represents a zone of maximum degree of colloidality, on either side of which hardness diminishes.[59]

The footnote on p. 532 of my paper, referred to by Professor Benedicks, refers to pure metals, where the isocolloidal zone naturally is narrow. In connection with the Pb–Sn alloys, where the metals differ materially in melting point, the following experiment is of interest. A strip of zinc immersed in a solution of $SnCl_2$ gives a coarsely crystalline tin tree, whereas lead under like conditions gives a lead tree. But if some lead-acetate solution is added to the $SnCl_2$ solution so that both Pb and Sn are thrown out simultaneously, the crystallization of both metals is much inhibited.

[56] Willows and Hatschek: "Surface Tension and Surface Energy," 28–32. 1919.

[57] *Trans.* (1919) **60**, 466.

[58] *Jnl.* Soc. Chem. Ind. (1920) **39**, 270R.

[59] See Zone of Maximum Colloidality, to be published in the *Jnl.* Am. Chem. Soc., 1921.

Nickel-chromium Alloys

By Leon O. Hart,* M. E., Harrison, N. J.

(Columbus Meeting, October, 1920)

The nickel-chromium alloys of importance are those containing iron and those free from iron. The most important alloys containing iron, with regard to high tonnage, are the nickel-chromium steels. Straight nickel steel was introduced about the year 1889, but it was not until 1895, when it was found that the addition of chromium greatly increased the

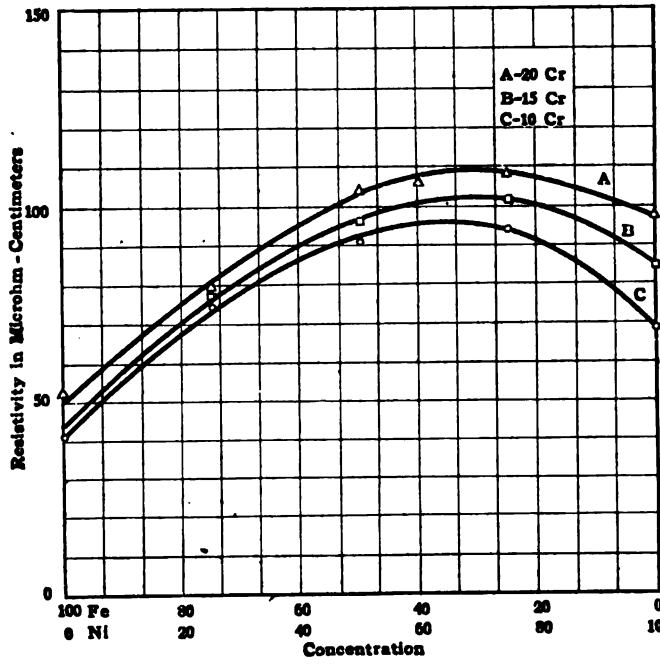

Fig. 1.—Resistivity of nickel-chromium-iron alloys.

strength and resistance to shock, that nickel-chromium steels came into use. The three types of nickel-chromium steels developed at this time were: Type 1, containing 3.50 per cent. nickel and 1.50 per cent. chromium; type 2, containing 2.00 per cent. nickel and 1.00 per cent. chromium; and type 3, containing 1.50 per cent. nickel and 0.50 per cent. chromium.

* Second Vice-president, Driver-Harris Co.

Type 1 steel is used principally for armor plate and projectiles. Types 2 and 3 were developed for the automobile industry, type 3 is admirable for drop forgings and makes an excellent case-hardening steel.

A nickel-chromium steel of type 1, containing 3.78 per cent. nickel, 1.60 per cent. chromium, 0.38 per cent. carbon, 0.28 per cent. silicon, 0.50 per cent. manganese, 0.035 per cent. sulfur, 0.025 per cent. phosphorus, when air hardened from 820° C., passed the following specifications:

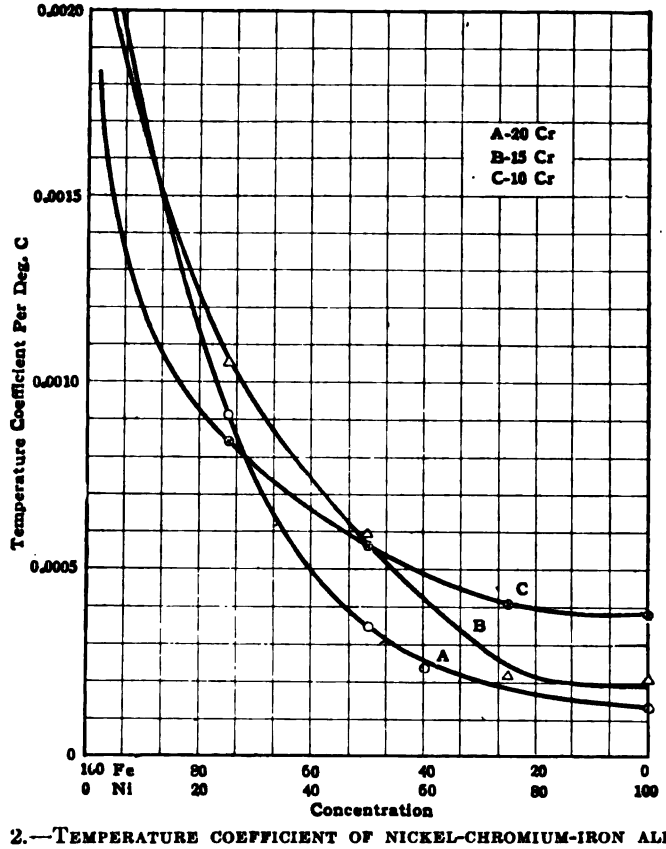

FIG. 2.—TEMPERATURE COEFFICIENT OF NICKEL-CHROMIUM-IRON ALLOYS.

Tensile breaking strength, minimum 220,000 lb. per sq. in.; yield ratio, minimum, 165,000 lb. per sq. in.; elongation, minimum, 5 per cent.; reduction in area, minimum, 13 per cent.; Brinell hardness number, 420.

Nickel-chromium-iron alloys having a much higher nickel and chromium content than the nickel-chromium steels just discussed were developed for electrical, heat, and chemical resistors. As early as 1866, research work was done by Mathieson for the British Physical Society to develop material for a standard ohm; this work was principally with copper-nickel alloys. In 1888, copper-nickel alloys were investigated by Feuss-

ner and St. Lindeck; Weston in this year developed manganin. In 1901, R. A. Hadfield investigated the electrical resistance of various nickel steels and found an alloy, containing 67.90 per cent. iron, 0.60 per cent. carbon, 1.50 per cent. manganese, and 30.00 per cent. nickel to have a specific resistance of 88.2 microhms per centimeter cube. All the metallic material developed for resistor material up to the year 1906, however, with the exception of platinum, oxidized badly at high temperatures. Platinum had a low initial resistance but a very high temperature coefficient so at high temperatures the resistance was great enough to make a fair heating element, but because of the scarcity and high price of platinum, only laboratory heating elements were possible. For commercial application a material that would resist oxidation at high temperatures, have a high initial resistance with a low-temperature coefficient, and be obtainable at a sufficiently low price was necessary. In 1906, Marsh found an alloy of nickel and chromium suitable for an electrical resistor and patented that application. From its use in household appliances, such as irons and toasters, the field has broadened until we have annealing furnaces of the car type, ovens for drying cores in foundries, and ovens for baking the enamel on automobiles. The General Electric

TABLE 1.—*Electrical Resistances and Temperature of Nickel-chromium-iron Alloys.* (M. A. Hunter.)

Nickel, Parts	Chromium, Parts	Iron, Parts	Resistivity, at 20° C. in Microhms per Cubic Centimeter	Temperature Coefficient, per Degree C., at 20° C.
100	25	0	99.79	0.00014
75	25	25	106.46	0.00024
50	25	50	97.00	0.00038
25	25	75	82.36	0.00090
0	25	100	43.68	0.00230
100	20	0	96.90	0.00012
75	20	25	108.04	0.00021
60	20	40	105.38	0.00023
50	20	50	103.67	0.00034
25	20	75	79.35	0.00091
0	20	100	52.07	0.00247
100	15	0	84.10	0.00020
75	15	25	101.30	0.00021
50	15	50	90.40	0.00059
25	15	75	76.88	0.001055
0	15	100	41.16	0.00233
100	10	0	67.80	0.00037
75	10	25	93.45	0.00040
50	10	50	95.94	0.00056
25	10	75	74.39	0.00084
0	10	100	41.13	0.00233

TABLE 2.—*Thermo-electric Force of Nickel-chromium-iron Alloys**

Alloy	Composition, in Parts			Hot-junction Temperatures, in Degrees C.				
	Nickel	Chromium	Iron	138	300	518	637	829
				Electromotive Force, in Millivolts				
A-11	75	10	25	0.87	0.78	−1.28	−2.99	−4.90
A-8	75	15	25	0.80	0.63	−1.23	−2.81	−4.47
A-1	75	20	25	0.86	0.88	−0.68	−1.95	−3.28
A-5	75	25	25	0.91	1.02	−0.36	−1.57	−2.77
A-25	50	0	50	6.25	11.45	12.54	11.05	10.46
A-12	50	10	50	1.43	2.11	1.14	0.16	−0.54
A-9	50	15	50	1.37	2.18	1.68	1.09	0.86
A-2	50	20	50	1.22	1.81	1.04	0.26	−0.27
A-6	50	25	50	1.29	2.00	1.46	0.76	0.33
				Hot-junction Temperatures, in Degrees C.				
				305	445	646	830	
A-26	25	0	75	Electromotive Force, in Millivolts				
A-13	25	10	75	8.50	13.69	14.48	14.57	
A-10	25	15	75	2.97	3.02	2.74	2.83	
A-4	25	20	75	2.98	3.00	2.78	2.94	
A-7	25	25	75	2.70	2.79	2.49	2.61	
				2.73	2.68	2.16	2.14	

* M. A. Hunter and J. W. Bacon: Thermo-electric Force of Some Alloys. *Trans.* Amer. Electrochem. Soc. (1918), **30**.

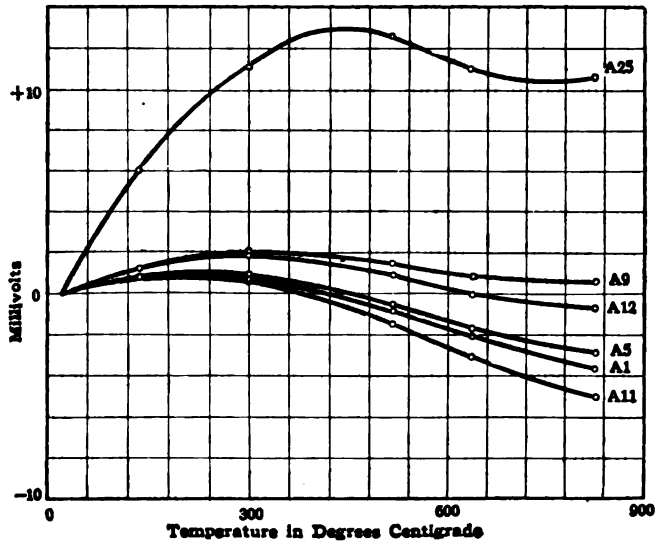

FIG. 3.—THERMO-ELECTROMOTIVE FORCE OF SOME NICKEL-CHROMIUM-IRON ALLOYS.

Co. is now producing very large heating units made of a nickel-chromium-iron alloy and the power used in the various elements, in this country, is estimated at 500,000 kilowatts. The low values obtained for the thermal electromotive force against iron, combined with the fact that most of the curves show inversion points, render these alloys useless for thermocouple work. Most of the values given in Tables 1 and 2 are shown on the curves of Figs. 3 and 4.

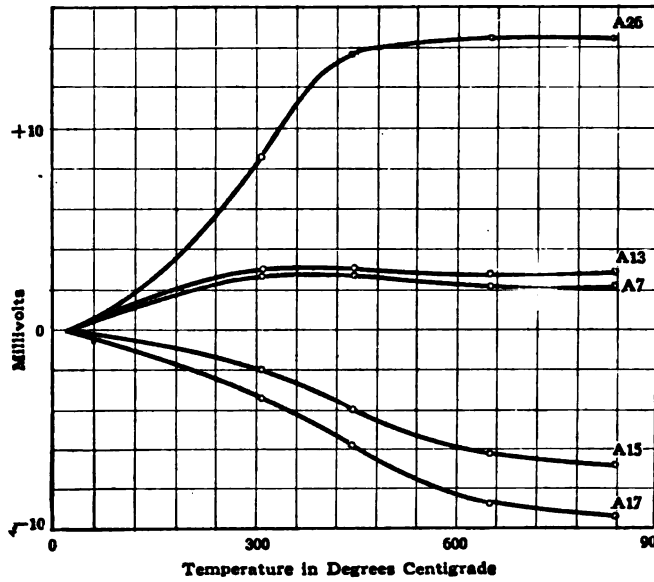

FIG. 4.—THERMO-ELECTROMOTIVE FORCE OF SOME NICKEL-CHROMIUM-IRON ALLOYS.

The most important commercial alloy of the nickel-chromium-iron group is that known as nichrome, manufactured by the Driver-Harris Co., Harrison, N. J. The cold-drawn nichrome is put on the market in the form of wire, ribbon, or sheet. It is used exclusively for electrical-resistance purposes and is approximately a 60 per cent. nickel, 12 per cent. chromium alloy containing about 25 per cent. iron and very low carbon. The electrical properties are: Specific resistance, 109.6 microhms per centimeter cube at 20° C.; 660 ohms per mil-foot at 20° C; temperature coefficient, 0.000170 ohm per degree C. per ohm at 20° C.; 0.000095 ohm per degree F. per ohm at 20° C.

The thermoelectric properties against nickel, as determined by Northrup, are:

TEMPERATURE, DEGREES C.	E. M. F. IN MICROVOLTS
100.0 water	2,303
232.0 tin	5,970
419.0 zinc	10,535
629.0 antimony	15,065
1082.6 copper	30,796

The physical properties of cold-drawn nichrome are:

Specific gravity, 8.15.
Weight per cubic inch, 0.29 lb.
Ultimate tensile strength, 102,200 lb. per sq. in.
Specific heat, 0.111 per degree C. over a range of 0° to 100° C.
Coefficient of linear expansion, 0.0000116 per degree C. over a range of 20° to 100° C.
Thermal conductivity 0.0326 calories per centimeter per second made with ¼ in. diam. section; this value is one-fifth that of soft iron.

Nichrome will stand a maximum operating temperature of 1800° F. (982° C.) and makes an ideal material for ordinary heating elements.

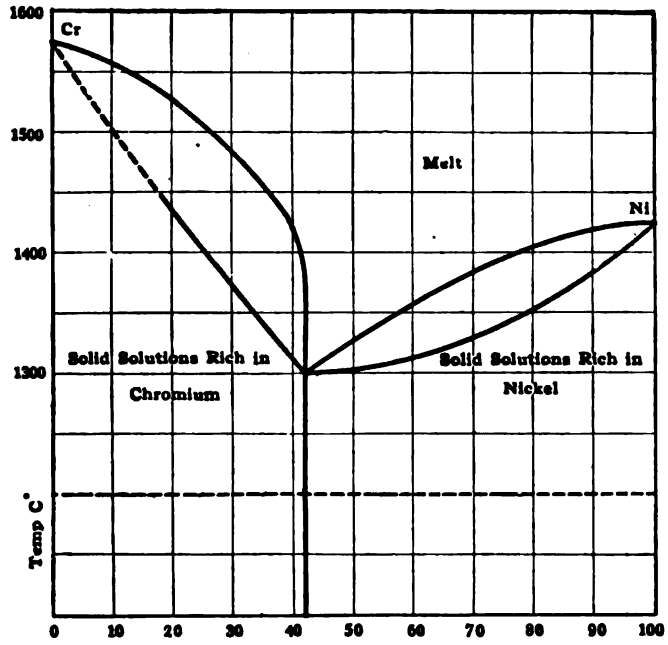

FIG. 5.—FREEZING-POINT DIAGRAM FOR NICKEL-CHROMIUM ALLOYS.

Forged nichrome has a higher carbon content than cold-drawn nichrome, being 0.60 to 1.00 per cent. It resists corrosion, does not oxidize and scale at high temperatures, and retains much of its strength at 800° C. It is not carbonized and is an ideal material for internal-combustion engine valves and for forged parts used in heating furnaces, such as conveyor chain links and carrier parts.

Cast nichrome has approximately the following analysis: nickel, 60.00 per cent.; chromium, 12.00 per cent.; iron, 26.00 per cent.; carbon, 0.60 per cent.; silicon, 0.40 per cent.; manganese, 1.00 per cent. It was developed primarily to replace the cast iron and steel containers for

metal parts that had to be heat treated. The life of these containers was short due to the rapid disintegration caused by oxidation, and consequent scaling, and also to warping. As these castings were made with heavy walls, the heat penetration at first was poor; but as the castings scaled away the heat penetration improved. As a result, if new and old pots were in the same furnace, the contents were often over or under heated.

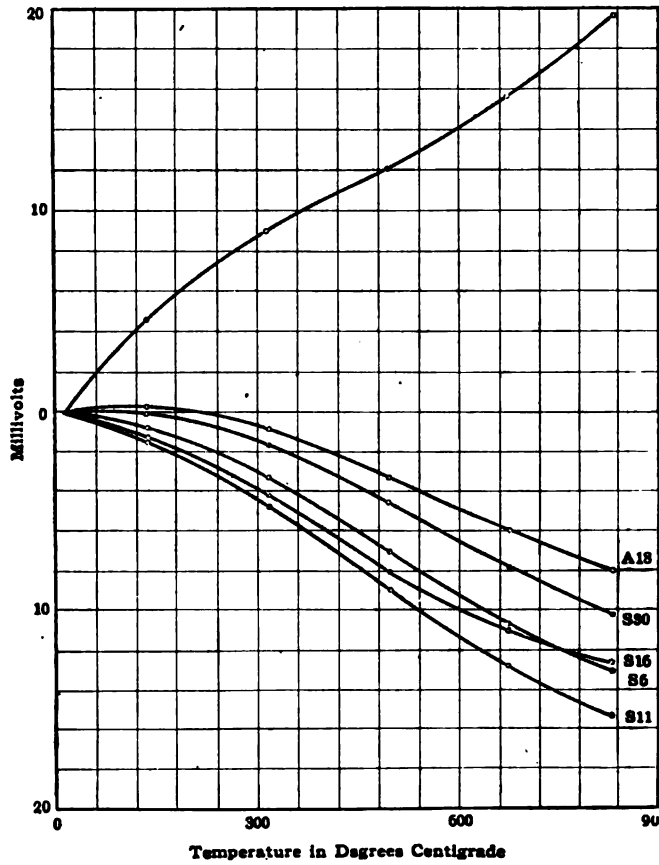

FIG. 6.—THERMO-ELECTROMOTIVE FORCE OF SOME NICKEL-CHROMIUM ALLOYS.

It was therefore desirable to use for these containers such material that the walls would be thin, but would maintain their thickness so that the heat penetration would be uniform. Then good results would always be obtained by heating to the same temperature. In addition, the price of the alloy per hour of service must not exceed that of the old container. J. C. Henderson developed and patented the alloy nichrome for these purposes; it is now being produced under the Henderson patents by the Driver-Harris Co.

Nichrome will not scale nor warp and is not brittle. It has been on the market less than five years but has come into general use for carburizing boxes, cyanide pots, lead pots, muffles and specially designed heat-treating apparatus. During the war, it was the only material that would stand up under the extreme conditions necessary in the production of the high-grade charcoal used in the gas masks of our soldiers. The retorts for the charcoal furnaces were castings 13 ft. 6 in. (4.1 m.) long and 15 in. (37.5 cm.) inside diameter, which were revolved at a speed of one revolution per minute in a furnace kept at a high temperature.

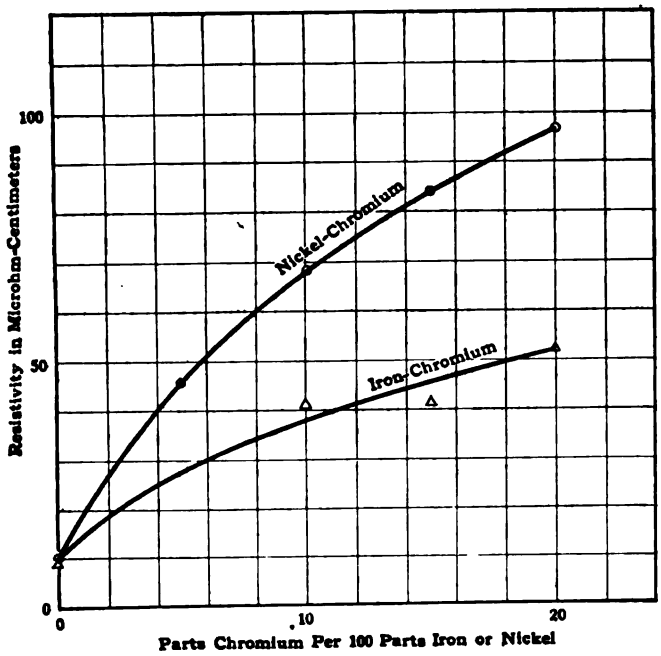

FIG. 7.—RESISTIVITY OF CHROMIUM ALLOYS.

The physical properties of cast nichrome are as follows:

Specific gravity	8.15	Softening point	2400° F.
Weight per cubic inch	0.29 lb.	Brinell hardness number	165–175
Melting point	2660° F.	Specific heat	0.111 at 100° C.

Coefficient of linear expansion 0.0000121 per degree C. with a temperature range of 0° C. to 100°. Length of specimen under test 92.3 cm.

Thermal conductivity 0.0341 calories per centimeter per second; or in a ratio of 1 to 4.88 of soft iron, or expressed in percentage 20.5 per cent. of the thermal conductivity of soft iron. This test was made with a 1-in. diameter section.

Ultimate tensile strength at 20° C.....	50,000 to 55,000 lb. per sq. inch
Yield point.....	40,000 lb. per sq. inch
Elongation.....	1.00 per cent.
Reduction in area.....	2.50 per cent.
Ultimate tensile strength at 800° C.....	24,500 lb. per sq. inch
Yield point at 800° C.....	20,100 lb. per sq. inch
Elongation at 800° C.....	4.00 per cent.
Reduction in area at 800° C.....	4.30 per cent.

Torsion test was made on a 230,000 in.-lb. machine.

Yield point was determined by drop of beam; test section was 8 in. long and 0.564 in. in diameter.

Torque at yield point 1300 in.-lb.; maximum, 3200 in.-lb. Stress in outer fiber at yield point 37,000 lb. per square inch; maximum 91,100 lb. per square inch.

Angle of twist at yield point 39° per foot; maximum, 1215; rupture, 1660.

Total elongation of outer fiber, 20.8 per cent.

Another important nickel-chromium-iron alloy, known as Nichrome II, has been developed by the Driver-Harris Co. for high duty work. Its maximum working temperature is 2000° F. (1095° C.). It is largely used in the form of heavy ribbon for the larger type of heating furnaces. Its analysis is: nickel, 65.0 to 67.0 per cent.; chromium, 20.0 to 22.0 per cent.; iron, 12.0 to 14.0 per cent.; manganese, 1.5 to 2.0 per cent.

It has the following electrical properties: Specific resistance, 116.3 microhms per centimeter cube at 20° C. or 700 ohms per mil-foot at 20° C. Temperature coefficient at 20° C. per degree F., 0.000096 ohm per degree per ohm; per degree C., 0.0000172 ohm per degree per ohm.

Nickel-chromium Alloys free from Iron

The nickel-chromium alloys free from iron are important in their ability to withstand oxidation and in their peculiar electrical properties. Alloys running from 100 to 70 per cent. nickel are completely homogeneous and are made up of large polygons of united crystals bounded by fine lines. Alloys containing 90 per cent. nickel and 10 per cent. chromium were completely non-magnetic at room temperature. A 2.0 per cent. chromium alloy lost its magnetism at 255° C.; pure nickel becomes non-magnetic at 355° C. The measurements of thermo-electromotive force, given in Table 4, were made against iron, the cold junction was maintained at 20° C. The curves, shown in Fig. 6, are approximately linear. The highest values for thermal electromotive force were obtained with an alloy containing 100 parts of nickel and 10 parts chromium. The electrical resistivity increases rapidly with the addition of chromium in the alloy and the temperature coefficient decreases. In resistance to

TABLE 3.—*Melting Point of Nickel-chromium Alloys**

Weight, Per Cent.		Temperature of Initial Freezing, Degrees C.	Temperature of Final Freezing, Degrees C.
Nickel	Chromium		
100	0	1452	
98	2	1450	1445
90	10	1445	1318
80	20	1430	1375
70	30	1402	1344
60	40	1377	1331
50	50	1322	1307
45	55	1318	1295
42	58	1290	
40	60	1345	1311
30	70	1507	1370
20	80	1545	
10	90	1550	
0	100	1553	

* G. Voss: *Zeit. anorg. Chem.* (1908) **57**, 34.

TABLE 4.—*Thermo-electromotive Force of Nickel-chromium Alloys*†

Alloy	Composition, Parts		Temperature of Hot junction, Degrees C.					
			135	311	492	667	706	834
	Nickel	Chromium	Electromotive Force in Millivolts					
....	100	0	4.39	9.00	11.93	15.54	.....	19.79
S-16	100	5	−1.35	−4.19	−8.13	−11.24	−11.76	−12.92
S-11	100	10	−1.61	−4.72	−8.98	−13.01	−13.70	−15.61
S-6	100	15	−0.92	−3.32	−7.06	−10.69	−11.38	−13.34
S-30	100	20	−0.20	−1.80	−4.75	− 7.83	− 8.45	−10.17
A-18	100	25	0.15	−1.00	−3.45	− 6.06	− 6.58	− 8.00

† By M. A. Hunter and J. W. Bacon: *Op. cit.*

TABLE 5.—*Electrical Resistances and Temperature Coefficients of Nickel-chromium Alloys*‡

Parts of Chromium per 100 Nickel	Resistivity Microhm-centimeter	Temperature Coefficient per Degree C. at 20° C.
0	10.7	0.00560
5	45.7	0.00097
10	67.8	0.00037
15	84.1	0.00020
20	96.9	0.00012

‡ M. A. Hunter and F. M. Sebart: *Jnl.* Amer. Inst. Metals (1917) **11**, 115.

oxidation at excessively high temperatures, they are more satisfactory than other binary combinations.

The Driver-Harris Co. makes an alloy bearing the trade name Kromore, which contains 85 per cent. nickel and 15 per cent. chromium. The specific

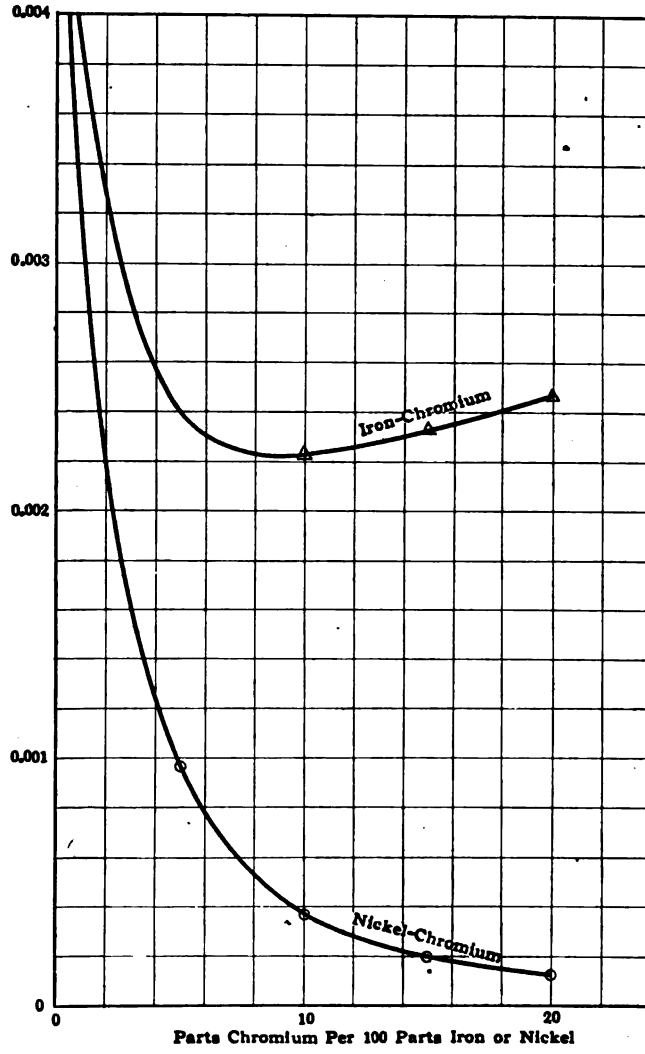

FIG. 8.—TEMPERATURE COEFFICIENT OF CHROMIUM ALLOYS.

resistance is 95.9 microhms per centimeter cube at 20° C. or 577 ohms per mil-foot at 20° C. The temperature coefficient is 0.000242 ohm per degree C. per ohm at 20° C. or 0.000134 ohm per degree F. This alloy resists oxidation to a high degree and is especially recommended when extreme conditions are to be encountered such as open type heating units. In

comparative tests made with wires suspended in air and heated to high temperatures by passing current through them, this material has stood up better than any known commercial resistance wire.

Kromore, Nichrome, and Nichrome II are made in electric furnaces of the Heroult type. The ingots are reduced by steam hammers to 2 in. square (5 cm.) billets from which ¼ in. (6.3 mm.) rods are hot rolled; from these rods, the material is cold drawn to wire or cold rolled to ribbon. For castings, the metal is poured into dry sand molds, and every casting is tested under 150 lb. air pressure before shipment. Only sound non-leakable castings are allowed to be shipped.

Treating Antimony Ores

BY GEORGE P. HULST,* EAST CHICAGO, ILL.

(Chicago Meeting, September, 1919)

PRIOR to 1914, there was little demand for antimony in this country; its use was limited almost entirely to the manufacture of type and bearing metals. Practically no antimony ore was mined here, the market being supplied principally from China, and the alloy was produced by a direct mixing of lead and antimony. The great world war, with its demand for shrapnel in hitherto undreamed of quantities, precipitated a great boom in the price of antimony. Nominally quoted at 6 c. to 7 c. in 1914, the price increased by leaps and bounds to 45 c. in March, 1916. Under the stimulus of high prices many small mines were opened, for it became profitable to work ores containing as low as 20 per cent. antimony. High-grade sulfide ores (stibnite), containing 55 per cent. to 60 per cent. antimony, were received from Bolivia, China, and Alaska. Low-grade sulfide ores, running from 20 per cent. to 45 per cent., were produced in Nevada, California, Idaho, Utah, and Mexico; much of this ore was fairly rich in silver. The principal oxide ores came from Mexico and Oregon. The following analyses are representative of various types of antimony ore:

	Sb	Pb	Cu	Ag	Au	SiO_2	Fe	S	CaO	Zn	As
Oxide ore.....	25.09					46.02	0.95	0.40	10.98	0.30	0.22
Sulfide ore.....	55.20					15.12	1.05	19.87		0.40	0.25
Sulfide ore.....	37.16	11.30	0.10	34.0		7.60	0.50	17.05	7.40	0.36	0.10
Sulfide ore.....	41.55	18.00	0.20	76.0	0.04	5.60	0.25	18.17	0.85	0.25	0.10

The International Lead Refining Co. fortunately was equipped to handle these ores through residue and blast furnaces. The charge consisted of a variety of sulfide ores containing Sb 20 to 60 per cent. and SiO_2 6 to 45 per cent., oxide ores containing Sb 20 to 40 per cent. and SiO_2 10 to 45 per cent. Secondary materials, such as battery plates, battery mud, lead oxide, paint, etc., together with refinery skims, softener skims, and other refinery byproducts, were treated along with the antimony ore to furnish the lead required. All silver-bearing antimony ores were treated in the residue furnace, the sulfur, iron, and copper forming matte that carried part of the silver, the balance going into lead bullion. The antimony slag produced was sufficiently low in silver to warrant being smelted in the blast furnace to antimonial lead.

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* Assistant General Manager, International Lead Refining Co.

The blast-furnace equipment consisted of two, five-tuyere, 42-in. round furnaces connected by flue to the bag house. On account of high zinc and arsenic in lead refinery byproducts, we ran a slag of the composition: SiO_2 26 per cent., FeO 40 per cent., CaO and ZnO combined 20 to 24 per cent. Net profit rather than metallurgy prompted a slag as low as possible in antimony even though the lead content was increased. Average analysis of slag for 6 mo. showed Sb 0.66 per cent. and Pb 2.36 per cent. Actual blast-furnace loss was 2.4 per cent. antimony and 1.503 per cent. lead. Due to sulfur and arsenic on the charge, some speiss was produced. The furnace charge varied from 2500 to 3000 lb. Coke ratio was 13 per cent. Blast pressure was maintained at 10 to 12 oz. The two furnaces smelted 60 to 90 tons of lead and antimonial material per day, producing 30 to 35 tons of antimonial lead of the following average analysis, Sb 13.00 per cent., Cu 0.15 per cent., As 0.75 per cent., Pb 86.1 per cent.

Chemical and Electrochemical Problems Involved in New Cornelia Copper Co.'s Leaching Process

BY HENRY S. MACKAY,* LONDON, ENG.

(Chicago Meeting, September, 1919)

THE interesting paper recently submitted by Messrs. Tobelmann and Potter[1] shows that chemical problems have developed which are of great interest in this new and important branch of metallurgy. Those who realize what a process of this kind really involves will agree that it deserves a better name than "leaching process." The word leaching conveys the idea that the copper is simply leached out of the ore with acid and then precipitated on iron; the chemistry of such a process would be of little interest. As, however, during the first year's operation of this plant 24,400,532 lb. (11,067,837 kg.) or about two-thirds of the produce, was electrolytic copper, while 7,992,033 lb., or about one-third, was cement copper, it would seem more appropriate to term the process electrochemical. It further appears, from the particulars given, that efforts have been made to have the entire production in the form of electrolytic copper. This could be done if the chemistry of the problem were kept in balance, so that it would not be necessary to discard any solutions that carried copper and acid of commercial value. A process, such as that under consideration, in which the copper is precipitated from solution by electrolysis, the solvent being at the same time regenerated, is one that requires special chemical and electrochemical knowledge and experience if all the copper in solution that has been extracted from the ore is to be successfully and economically produced as electrolytic copper.

The object of this paper is to discuss, from the practical and theoretical standpoints, the chemical and electrochemical problems involved in the working of a process of this kind, and which must be solved to keep it in chemical and electrochemical equilibrium. In such a process, if the chemical balance is maintained, a solution can be used alternately as a solvent for the copper in the ore and as an electrolyte of high efficiency for the precipitation of the copper. To maintain the chemical equilibrium and so attain this result, the process must be so controlled that the solu-

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[1] *Trans.* (1919) **60**, 22.

tion will not take up from the ore injurious impurities to such an extent that it will lose its efficiency (either as a solvent or as an electrolyte) and necessitate the discarding of any part of the solution in order to rid it of the impurities. The chemistry can be kept in balance if the following important practical points are thoroughly understood and controlled:

1. Carefully analyze and prepare the ore for treatment.
2. Use a weak acid solution as a solvent and cause it to carry sufficient copper to make it an electrolyte of high efficiency.
3. Leach the ore in such a way that the maximum amount of copper will be dissolved in the shortest time with the minimum extraction of impurities.
4. Regulate the flow of solvent through the ore in such a way that the metals in solution, like iron and aluminum, combined as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$, will be precipitated and automatically removed from the field of action, and the combined acid recovered.
5. In washing the leached ore charge, use only the minimum amount of water to get the maximum soluble-copper recovery by replacement and not by dilution. Never use acid solutions in washing.
6. Standardize solutions before electrolysis by mixing solutions low in acid and high in copper with those low in this metal and high in acid to obtain a standard electrolyte of high efficiency.
7. As required, use solutions as solvents after they have become neutral.

Analysis and Preparation of Ore for Treatment

When the problem is to treat an oxidized copper ore, the ore must be analyzed to determine the elements it contains and also the proportion of each that will be dissolved in the chemical solutions used as the solvent for the copper. A perfect understanding of this step is the basis on which the whole chemical working of the process depends. It must also be determined definitely, by experiment, to what degree of fineness the ore must be crushed to extract, with the solvent it is proposed to use, the maximum percentage of copper and the minimum percentage of impurities in the shortest time without agitation.

The most economical solvent is a sulfuric-acid solvent, carrying not more than 2 per cent. sulfuric acid, used in a continuous flow, as this solvent requires the minimum acid consumption in the plant and extracts the maximum copper and the minimum impurities.

It is ordinarily assumed that an oxidized ore is ideal for treatment when the copper readily dissolves from the ore in a sulfuric-acid solution. On the contrary, to find an oxidized copper ore that will be ideal to treat

by an electrochemical method would be most unusual, for oxidized ores generally carry soluble iron in excess of what can be economically controlled without roasting. Ores are only properly prepared for electrochemical treatment by roasting, the soluble impurities being controlled definitely in the roasting. The whole process is thus simplified, for, in addition to controlling the molecular combination of metals with sulfur and oxygen, the solvent required in the process can be produced in the same operation by properly roasting the ore in the presence of sulfur.

The ores being treated by the New Cornelia Copper Co., at Ajo, Ariz., are oxidized ores and would not appear to be ideal to treat by an electrochemical process, judged by the results of the first year's operation of this plant. It appears, however, that by altering its preparation, as was done in the experimental test No. 3,[2] the ore can be made eminently suitable for electrochemical treatment. The average analysis of the ore shows that, before treatment, it carried 5.05 per cent. iron and after treatment, 4.33 per cent., showing an extraction of 0.72 per cent. This soluble iron is greatly in excess of what it should be and was the principal cause of the disturbance of the chemical equilibrium of the process. This iron continually accumulated until the solution carried over 2 per cent., when it so interfered with the electrochemical part of the process that about one-third of the solution passing through the plant had to be discarded to keep this part of the process in balance.

The importance of controlling the soluble iron in the ore is apparent when an extraction of only 0.72 per cent. iron made it necessary to discard during the year solutions that contained 7,992,033 lb. of copper. Besides, including the acid bought and generated by the sulfur-dioxide plant, there appears to have been about 75,000 tons of 100-per cent. acid in this discarded solution as free and combined acid, as approximately 75,000 tons of 100-per cent. sulfuric acid were used in the process for the first year over and above what was regenerated by electrolysis. This excess iron passing into solution from the ore seems to have been partly due to the ore not being properly prepared for treatment: finer crushing would apparently have greatly improved the chemical balance.

The summary of results of the process[3] shows that 41.9 per cent. of the ore treated would not pass a 4-mesh screen, and the summary of results to Jan. 1, 1919, shows that of the average ore treated 27.01 per cent. would not pass a 3-mesh screen. It will probably be found, by proper analysis and experiment, that the ore was much coarser than is required for the best results in electrochemical treatment. Crushing to a fineness sufficient for extraction and percolation may not be suitable for an electrochemical process, where the chemistry of the process is the main controlling factor. In the latter case the ore must be crushed to

[2] *Op. cit.*

[3] *Op. cit.*, Table 1.

the proper fineness, and must be so bedded in the leaching tanks that the maximum extraction may be obtained in the minimum time without agitation.

If the ore is not crushed sufficiently fine, in leaching, the copper is quickly dissolved on the outside of the coarser pieces and slowly on the inside. This gives the acid in the solution a longer time to attack the iron and other base elements, which are in excess on the outside of the larger ore particles after the copper has been dissolved. As a result, more iron goes into solution than there would if the ore had been more finely crushed. In the latter case the copper would be dissolved from the center of the particles more quickly, and so the time in which the acid would be in the presence of iron and other base elements in excess on the outside of the particles would be shortened.

At this step the chemical reactions that take place are governed by the law of chemical affinity, which is the chemical foundation of the whole process. This law is well known, but its importance may not be realized and it may not be used to the fullest extent in connection with the electrochemical treatment of copper ores. It governs the formation and decomposition of metal sulfates and is, therefore, the basis for: the roasting of copper ores containing iron and other metals in the presence of sulfur; the leaching with sulfuric acid of ores containing copper, iron, and other metals; and the precipitation by electrolysis of copper from sulfate solutions carrying other metals.

In leaching with sulfuric acid, sulfates of copper can be formed from ore containing other metals without forming sulfates of the other metals, if the soluble copper in the ore is kept in excess of the other soluble metals. The reason for this is that, when two or more metal oxides are in the presence of a weak solution of sulfuric acid, sulfates of the metal with the lowest molecular heat of formation will form first, and as long as this metal oxide is in excess very little of the other metal sulfates will form. Similarly, copper can be precipitated from sulfate solutions containing other metals (such as iron, aluminum, zinc, etc.) by always keeping sufficient copper in the electrolyte so as not to increase the voltage to equal the decomposition voltage of any of the other metals in the solution, as the electromotive force is proportional to the chemical affinity.

The principal metal sulfates in the problem under consideration, with their molecular heats of formation, are as follows: $CuSO_4$, 197,500 cal.; $FeSO_4$, 234,900 cal.; $Fe_2(SO_4)_3$, 650,500 cal.; $Al_2(SO_4)_3$, 879,700 cal.

This selective action of a weak acid solution is indicated in the experimental test No. 3, the results of which are shown in the accompanying table taken from Messrs. Tobelmann and Potter's paper. In this instance the ore was crushed finer than that treated in the large plant for the first year and permitted the solution to act under more favorable conditions. The copper was dissolved before the weak solution had time

to act on the iron and other impurities. In this test the ore was crushed to minus 6-mesh plus 8-mesh screen and gave the following results in pounds of material dissolved per ton of ore treated: 91.50 per cent. of all

Data from Paper by H. A. Tobelmann and J. A. Potter

	Leaching Hours				
	12	24	36	60	72
Cu	18.20	21.10	22.50	22.60	23.40
Fe	0.70	1.00	1.15	1.55	1.85
Al_2O_3	1.69	2.28	2.59	2.88	3.01
MgO	0.26	0.34	0.37	0.31	0.42
CaO	1.27	1.18	1.08	1.08	1.08
P_2O_5	0.25	0.37	0.43	0.76	0.83

the copper in the ore was extracted in 3 days and only 0.09 per cent. of the iron was dissolved from the ore and 0.15 per cent. of the alumina. Presuming that this test was carefully made on a representative sample of the ore, there appears no reason why it cannot be repeated in the large plant. In that event, this ore would be ideal for electrochemical treatment without roasting, because 0.09 per cent. iron soluble in the ore is not enough to interfere seriously with the electrochemical equilibrium of the process if the other chemical problems are properly controlled.

Chemical Control of Solvent and Electrolyte by Methods of Leaching

In the chemical problem involved in leaching copper ore, where copper is to be precipitated by electrolysis, the strength of the acid solvent is one of the most important factors. In Table 13, Messrs. Tobelmann and Potter give the average analysis of some 30,000 to 35,000 tons of solution at all times on hand and passing through the plant. The average free-acid strength of this solution is 1.50 per cent. sulfuric acid, which is a good average acid strength for a solvent and electrolyte to be used in an electrochemical process; it should never exceed about 2 per cent. in any part of the process. This weak acid solution was the main factor in the process, which kept the soluble iron and other impurities in the solution to a point where they could be partly controlled as they were by the methods employed.

There were, however, periods when the acid strength of the solvent was raised to 3 per cent.; this was used on the oldest charge, that is, when the impurities were in excess of copper. Fewer impurities would have been dissolved, less acid consumed, and a better electrolyte maintained if the maximum free-acid strength of the solvent had not exceeded 2 per

cent. The chemical reason for this is that, in leaching the ore, the more even the balance, as between the soluble copper and the acid present, the more ideal are the conditions produced for the sulfate of copper to form in preference to the other sulfates, which require greater molecular heat of formation.

With a 2-per cent. acid strength of solvent leaching an ore containing 2 per cent. or less of copper and properly prepared, the acid so quickly combines with the copper to form the sulfate that the free acid in solution soon becomes so weak that it no longer remains a solvent for iron and the other metals that require a higher molecular heat to form their sulfates. It will, however, continue to act as a solvent for copper until it becomes neutral.

In leaching an ore prepared so that it contains not more than 0.10 per cent. soluble iron and not more than 0.20 per cent. aluminum, a 2-per cent. acid solution that has been used alternately for a long period as a solvent and an electrolyte will take up in the plant not more than about 0.50 per cent. total iron and 0.75 per cent. total aluminum, provided that the solutions are, at certain periods, used after they become neutral. At about this point in the life of a solution, the accumulations of these metals as sulfates in the solution increase to a point where part of the iron in solution is oxidized by the electrolysis so that it combines as ferric sulfate $Fe_2(SO_4)_3$. Ordinarily, about one-half of the total iron, or a little less, will be in the form of ferric sulfate. The proportion depends a good deal on the speed at which the electrolyte flows through the electrolytic vats when the copper is being precipitated. All of the aluminum is combined as $Al_2(SO_4)_3$.

When ferric sulfate is formed in the solution, combined with about 0.25 per cent. iron, it will act as a solvent for copper when the solutions become neutral. Aluminum sulfate also will act as a solvent in neutral solutions when the alumina reaches about 0.50 per cent. When these sulfates accumulate until they reach these percentages in the solution they become a solvent and are precipitated when the solution is used without free acid. They give the following chemical reaction in the presence of copper oxide:

$$3CuO + Al_2(SO_4)_3 + 3H_2O \rightarrow 3CuSO_4 + 2Al(OH)_3$$
$$3CuO + Fe_2(SO_4)_3 \rightarrow 3CuSO_4 + Fe_2O_3$$

Apparently this reaction of ferric sulfate and copper oxide has an end reaction caused by hydrolysis of the ferric oxide in an aqueous solution, which end reaction is probably as follows:

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe(OH)_3$$

This end reaction apparently takes some time to form and, therefore, the longer the precipitates from the primary reaction are left in the ore

the more soluble is the iron precipitate, as it is very slightly soluble in weak acid in the form of Fe_2O_3.

The primary reaction precipitates the ferric oxide or the aluminum hydroxide from the solution into the ore charge, and the oxides and hydroxides are discarded with the ore tailings. In this way, when the copper is deposited by electrolysis, the acid, combined with the aluminum and iron sulfates in the solution, is recovered from the copper sulfate formed by these solvents, the iron and aluminum are automatically removed from the solution, the acid is recovered, and the chemical equilibrium maintained. This result is brought about in the practical operation of a plant when the ore is prepared so that it carries not more than 0.10 per cent. soluble iron and is crushed to the proper fineness to leach in the shortest time. The solvent must carry not more than 2 per cent. free acid, and must be used as a solvent in certain periods after it becomes neutral. Under these conditions the iron and aluminum are precipitated from the solution faster than they can accumulate.

In treating an oxidized ore, when the first condition cannot be fulfilled because the ore carries excess soluble iron, there are three methods of procedure to maintain a chemical equilibrium:

1. Make the iron in the ore insoluble by roasting.

2. If the iron is not greatly in excess, and to save the cost of roasting, a special ore charge carrying copper-oxide should be leached with a neutral solution carrying $Fe_2(SO_4)_3 + Al_2(SO_4)_3$ and not followed by an acid solution. This special ore charge should be so proportioned that the accumulations of the aluminum and iron precipitates from the solutions will not interfere with the percolation of the ore before the copper is extracted. If the ordinary low-grade ore being treated does not carry sufficient copper oxide to precipitate the iron and aluminum from the solution fast enough to maintain the chemical equilibrium, this special ore charge should be enriched with roasted copper concentrates to produce oxides to be added to the ore charge. In this way, the required reactions take place to purify the solution, and the ore charge, acting as a filter, by downward leaching leaves behind the iron and aluminum precipitated from the solution. These will be discarded with the ore tailings, so that the solution is clear of all sediment when standardized with acid.

3. The same result can be obtained, with soluble iron greatly in excess, by agitating with air finely ground copper-oxide ore in the neutral solutions, but by this method the solutions need to be clarified by filtering after agitation.

The experiments made at the New Cornelia Copper Co.'s plant to precipitate the iron and aluminum on the ore charge by this method appear to have failed, because, first, the ore was not properly prepared so that the solvent would extract the minimum iron from the ore; second, there

were periods in the leaching when the solvent carried too high a percentage of free acid, resulting in excessive iron going into solution from the ore; third, in leaching, acid solutions followed neutral solutions on the ore charge, which they should not do when the soluble iron is greatly in excess.

Leaching the Ore Charge

The depth of the ore charge to be leached, when the copper is to be precipitated from he solution by electrolysis, varies with the class of ore to be treated. The problem is not the same as the one involved in the ordinary leaching process, where the copper is to be precipitated on iron. In the former, the problem is to get the highest extraction in the shortest time to prevent the solvent from taking up excessive impurities. In the latter, the chemistry of the problem is not so important, and extraction and percolation are the points generally considered in determining the depth of the ore charge. In each problem it is a matter of experiment to determine the depth of the ore charge, as the conditions vary with different classes of ore. This experiment should take into consideration the degree of fineness to which the ore should be crushed and the method and depth of bedding of the ore charge in the leaching tank that will enable the solvent to extract the maximum copper in the minimum time.

It is a good practice to bed the ore charge in the tanks in a neutral solution, starting with about 1 ft. of solution in the bottom of the tank, and gradually increasing this solution as the ore is added, until the tank is charged, bringing the solution to the top of the ore when the charging is completed. In this way the ore is thoroughly saturated with the solution before leaching begins. This tends to prevent the ore from channeling, and a smaller amount of dust will be formed than if dry ore were charged into the tanks. A neutral solution is desirable when excessive iron is soluble in the ore, as an acid solution remaining on the ore for the time required to fill the tank would take up a certain amount of the impurities soluble in the solution.

In the New Cornelia Copper Co.'s plant, the leaching solutions pass in at the bottom of the ore, rise through the ore, and pass out at top. This method has a tendency to wash out fine particles of ore, which are carried off in the acid solution to the settling tanks. The impurities in the fine ore particles are in a favorable condition to be dissolved by the acid solution in the settling tanks, and so the undesirable elements in the solution are increased. In some ores, slimes settle slowly in solutions heavier than water and are therefore carried from the settling tanks into the electrolytes, where they are objectionable. Where the ore is leached in a downward direction, all slimes are eliminated, because the ore acts as a filter and the solutions come off clear at the bottom of the tanks and there is nothing to foul the solution after it leaves the ore.

Washing the Ore Charge

Table 4 in Messrs. Tobelmann and Potter's paper (reproduced here) gives the analyses of the wash waters used in washing the ores at the Ajo plant. It will be noticed that three of the wash waters used carry free acid.

Table 4.*—*Analyses of Wash Waters for March*, 1918

	Solution Off	First Wash	Second Wash	Third Wash	Fourth Wash
Free H_2SO_4, per cent	2.56	1.02	0.68	0.48	0.10
Copper, per cent	2.40	1.61	1.15	0.74	0.38
Ferrous iron, per cent	1.58	1.06	0.70	0.47	0.04
Ferric iron, per cent	0.72	0.48	0.31	0.17	0.26
Specific gravity	1.30	1.20	1.13	1.08	1.05

* From paper by Messrs. Tobelmann and Potter.

The method adopted in washing the copper solutions from the ore residues in this plant is first to allow the ore residues to drain thoroughly, then to apply the wash waters used in the order shown in the table, starting as a first wash with the previously used wash solution containing the free acid and metals combined as sulfates (as shown in the third column) and as a second wash with the solution shown in the fourth column, and as a third wash, with the solution shown in the fifth column, and a fourth wash of clear water. After the first wash water had passed through the ore residues, the tank was allowed to drain thoroughly before the next wash water was applied. By this method, the copper-bearing solution remaining in the ore residues is gradually diluted until the wash with fresh water comes off containing free acid and metal sulfates, as shown in the fifth column of the above table. This method of washing tends to throw the process out of equilibrium for it tends to foul the solution, it produces excessive dilute solutions in the plant, and it leaves too much dissolved copper in the residues.

When a copper ore carrying iron is leached with an acid solution until the soluble copper is removed, leaving the iron greatly in excess in the residues, and the air is allowed to come in contact with the freshly leached ore, the iron rapidly oxidizes and becomes partly soluble in weak acid. When an acid solution is used to wash the ore after it has been thoroughly drained and the air has been allowed to take the place of the solution, the iron that is oxidized is attacked by the acid and it is dissolved in the solution. The oftener these acid washes are repeated in this manner, air being allowed to pass into the residues between the different acid solution washes, the more iron is dissolved. To prevent this, the air should not be allowed to come in contact with the ore until

after it is leached and washed, and acid solutions should never be used as wash waters.

In an electrochemical process, it is necessary not only to keep impurities from accumulating in the solution but also to keep the solution from accumulating in the plant. Therefore, the problem is to wash the dissolved copper out of the leached ore as thoroughly as possible without increasing the volume of the solution or the impurities in the solution. This can be done very completely by replacing the solution containing the copper and acid in the ore, after leaching, by fresh water in the following manner: When the ore is leached and the solution drawn down until it begins to disappear below the top of the ore, close the solution outlet at the bottom of the tank and add fresh water at the top of the ore, at first gently, to prevent the water and solution mixing, and, after there is a few inches of water on the top of the ore, the flow of the water can be increased gradually, until the weight of the water added is equal to about 20 per cent. of the weight of the ore charge. Then open the solution outlet at the bottom of the tank and allow the solution to run a little slower than the normal leaching flow. In this way, under proper conditions, the column of water on top of the solution in the ore will replace the solution, so that the residues, when thoroughly drained, will carry not more than 0.02 per cent. water-soluble copper or 0.40 lb. (0.18 kg.) copper per ton of ore. The amount of water that it is necessary to add to replace solutions in this way varies somewhat according to the character of the ore and the degree of fineness to which it has been crushed. The economical amount that is to be added must be determined by experiment. In the practical operation of a plant, it has been found by the writer that the economical amount is from 18 to 23 per cent. of the weight of the ore, 20 per cent. being a fair average. Whether all this wash water can be added to the stock solution or not depends on the solution losses in the plant.

The loss of solution in the Ajo plant by evaporation was from 5 to 10 United States gallons per ton of ore, or an average of 7.5 gal., which would equal 3.12 per cent. of the weight of the ore. As the average moisture of the residues for the year was 11.12 per cent., the evaporation and the moisture in the residues will equal a solution loss of 14.24 per cent. of the weight of the ore. In this case, the difference between 20 per cent. water added and the net loss of solution would be 5.76 per cent. of the weight of the ore treated. It would be necessary to discard this quantity of the wash water (or 12.50 U. S. gal. per ton of ore treated) so as not to increase the volume of solution in the plant. The wash water to be discarded should be taken from the last part of the washing and final draining of the residues. This can best be arranged by running the solution being replaced from the residues into a sump tank having a water gage to regulate the amount of the solution drawn off. The

volume of this surplus solution would be small and it would carry very little copper and free acid, but what it did carry in copper could be recovered by precipitation on iron, or it could be evaporated down to a point where it could be precipitated by electrolysis.

On account of its dry climate, Arizona is an ideal location for a plant for the treatment of ores by electrochemical methods. To get the maximum evaporation for the solution all tanks that are to contain solutions should be constructed so as to have the greatest surficial area possible without interfering with the other practical problems involved in plant construction. It would probably be possible to construct a plant in Arizona so that the evaporation of the solutions would be sufficient, together with the solution losses in the plant and the moisture in the residues, to equal the wash waters added.

Electrolytic Deposition of Copper from the Solution

Table 17 (reproduced here) gives the analyses of the solution entering and leaving the electrolytic tank-house of the Ajo plant: The solution

Table 17.—*Analyses of Sloution Entering and Leaving Tank House*

	Solution to Tank House Neutral Advance, Per Cent.	Solution from Tank House Acid Advance, Per Cent.		Solution to Tank House Neutral Advance, Per Cent.	Solution from Tank House Acid Advance, Per Cent.
Cu	2.985	2.513	MnO	0.040	0.040
Fe (ferrous)	2.315	1.660	CaO	0.060	0.062
Fe (ferric)	0.085	0.745	P_2O_5	0.130	0.130
Fe (total)	2.400	2.405	Cl	0.0123	0.0110
Al_2O_3	2.470	2.465	H_2SO_4, free	1.70	2.10
MgO	1.360	1.360			

with the average analyses used as an electrolyte in the precipitation of copper gave a low efficiency principally because of the excess iron present. The total iron in the solution is 2.40 per cent. combined partly as ferrous and partly as ferric sulfate. Before this solution entered the electrolytic tanks, the ferric iron had been reduced by sulfur dioxide until it was only 0.085 per cent.; but during electrolysis the iron combined as $Fe_2(SO_4)_3$ increased to 0.745 per cent. The current losses in oxidising the iron from 0.085 to 0.745 per cent., a difference of 0.660 per cent., together with the loss of copper dissolved by the ferric sulfate formed, reduced the efficiency of the electrolyte, and the average copper deposited per kilowatt-hour by the direct current passing through the electrolyte was, as a result, only 0.82 lb. Taking the average electromotive force for the year as 2 volts, 0.82 lb. of copper per kilowatt-hour would repre-

sent a current efficiency of only 62.90 per cent. of the theoretical based on Faraday's law.

It is not possible to maintain an average current efficiency of 100 per cent., because of imperfect electric contacts in the metal conductors, short circuits between the electrodes by sprouting, etc.; but in a plant properly designed and operated so that the total iron in the electrolyte will be not more than 0.50 per cent., a current efficiency of from 85 to 90 per cent. should be attained, which would give about 1 lb. copper per killowatt-hour.

The other base elements in the solution, as shown in Table 17, are of much less importance, because in the presence of copper and acid none of these will be precipitated if, by retaining sufficient copper in the electrolyte, the voltage is not increased to equal the decomposition voltage of any of the other metals in the electrolyte. For this reason it is always necessary to carry excess copper in the solution.

In the operation of the plant for the first year this was provided for, and Table 17 shows that the average copper carried in the electrolyte was 2.749 per cent. and that the average copper precipitated from the electrolyte in passing through the electrolytic vats was 0.472 per cent. This was the controlling feature of the electrolyte used, and without carrying this excess copper in the electrolyte very little, if any, of the copper from these foul solutions could have been economically produced as electrolytic copper. The percentage of copper carried should be more in a foul electrolyte than in a good standard one, and should always be in excess of the percentage of the metal sulfate present, which has the lowest molecular heat of formation next above copper sulfate (in this case $FeSO_4$). The percentage of copper carried should also be proportioned to the current density used, as the copper in the electrolyte must be sufficient to carry the current so as to keep the electromotive force as near as possible to the decomposition voltage of copper sulfate.

In an electrolyte carrying not more than 0.50 per cent. total iron, with a current density of from 10 to 14 amp. per sq. ft. of cathode surface, good efficiency will be given if, on entering the vats, it carries 2.00 per cent. copper and 1.40 to 1.60 per cent. free acid. The percentage of copper precipitated from the solution that passes through the electrolytic vats should be from 0.30 to 0.40 per cent. and the rise in free acid the equivalent, or from 0.465 to 0.620 per cent. If an electrolyte of this composition is maintained in the plant at a temperature of 40° C. a current efficiency of over 90 per cent. will be maintained.

The solutions, before they are used as electrolytes, should be standardized by mixing those high in copper and low in acid with those low in copper and high in acid. To get the best efficiency and the required acid for the solvent for the copper in the ore, the rate at which the electrolyte should flow through the vats should be governed in accordance with the

current density used, the required degree of oxidation of the iron in the solution, and the percentage of copper to be deposited. To increase the flow with a fixed current density diminishes the amount of copper deposited, acid formed, and iron oxidized, per gallon flowing. To diminish the flow increases the acid formed, the amount of copper deposited, and the iron oxidized in the solution. This adjustment governs the electrochemical equilibrium of the process.

The results of one of the experiments made by the writer to determine the current efficiency of an electrolyte containing varying amounts of iron are given in the accompanying Table 1.

This experiment shows that, with the voltage used, in order to deposit 1 lb. (0.45 kg.) copper per kilowatt-hour, the electrolyte should carry not more than 1 per cent. total iron.

Conclusions

The successful operation of an electrochemical process for the treatment of copper ores depends almost entirely on the attention given to conditions that affect the chemistry of the process. The points in the process of the New Cornelia Copper Co. that have been discussed in this paper are the controlling factors, and, when these have been adjusted, there is nothing to prevent the successful and economical production of electrolytic copper from all the solutions produced in the plant.

When the chemical and electrochemical equilibrium of the process have been adjusted, the acid consumption (over what will be regenerated in the plant) will not exceed 30 lb. (13.6 kg.) of 100 per cent. H_2SO_4 per ton of ore treated, or a saving (based on the estimated consumption per ton of ore for the first year) of about 73 per cent., or about 55,000 tons of 100 per cent. H_2SO_4 per annum. (The figure taken for the first year includes the acid bought from outside, together with that generated in the sulfur-dioxide plant, after deducting the amount regenerated by electrolysis.)

When the adjustments have been made and the process controlled so that the solution will carry not more than 0.50 per cent. iron, the current efficiency will be not less than 90 per cent. of the theoretical. The saving in power in the New Cornelia Copper Co.'s plant under these conditions, using an electromotive force of 2 volts would be 366 watt-hours per pound of copper, which calculated over 24,400,532 lb. of copper deposited in the first year, would be 8,930,595 kilowatt-hours. With the total iron in the solution about 1.00 per cent., the current efficiency will be about 85 per cent. of the theoretical, and at this efficiency 1 lb. of copper can be deposited per kilowatt-hour with a current density as high as 14 amp. per sq. ft. of cathode surface, and with an electromotive force of 2.20 volts. The saving in power that would result under these conditions would be 219 w.-hr. per lb. of copper, or 5,343,716 kw.-hr. on the

TABLE 1.—*Tests Made to Determine the Effect of Varying Amounts of Iron in the Electrolyte, using Lead Anodes*

Test No.	Assay before Electrolysis				Assay after Electrolysis				Current Efficiency, Per Cent.	Watt-hour per Pound Copper Deposited	Average E.m.f., Volts	Current Density, Amperes per Square Foot of Cathode Surface	Average Temperature, Degrees C.	Time of Test, Hours	Remarks
	Fe'', Per Cent.	Fe''', Per Cent.	Cu, Per Cent.	H_2SO_4, Per Cent.	Fe'', Per Cent.	Fe''', Per Cent.	Cu, Per Cent.	H_2SO_4, Per Cent.							
1	0.25	0.20	2.47	1.96	0.14	0.31	1.71	3.08	92.00	880	2.198	14.50	42.0	2	Air circulation.
2	0.47	0.44	3.13	1.50	0.40	0.52	2.07	3.10	86.00	950	2.145	14.60	41.6	3	Air circulation.
3	0.61	0.71	3.13	1.50	0.62	0.70	2.23	2.80	68.70	1260	2.280	15.00	42.6	3	Air circulation.
4	0.67	0.63	3.15	1.50	0.40	0.90	2.27	2.79	67.50	1290	2.285	15.00	43.5	3	Not circulated by air.
5	0.82	0.60	2.85	1.50	0.82	0.60	1.97	2.80	69.70	1360	2.430	14.60	44.0	3	Air circulation.
6	0.90	0.82	2.97	1.50	0.60	1.02	2.05	2.62	72.50	1188	2.245	14.60	44.0	3	Air circulation.
7	0.97	0.75	3.06	1.50	1.00	0.73	2.12	2.95	70.00	1415	2.235	14.43	44.6	3½	Air circulation.
8	0.40	1.12	3.25	1.50	0.54	1.04	2.37	2.86	69.02	1182	2.136	14.33	41.8	3	Air circulation.
9	1.47	0.07	2.94	1.50	0.81	0.73	2.26	1.61	65.00	1225	2.030	14.40	44.8	2¾	Air circulation.
10	1.00	0.08	3.17	1.50	0.40	0.58	2.05	2.48	84.00	1015	2.235	14.43	45.2	3½	Not circulated by air.
11	0.94	0.08	3.52	Nil.	0.52	0.50	1.86	1.86	84.50	1120	2.490	15.00	44.0	4½	Not circulated by air.
12	0.54	0.04	3.06	Nil.	0.22	0.35	1.61	2.12	91.70	995	2.400	13.60	45.4	4	Not circulated by air.
13	0.26	0.02	3.06	Nil.	0.12	0.16	1.51	2.26	97.50	920	2.380	13.60	45.8	4	Not circulated by air.

first year's operations. When the chemical problems are controlled by the means described, the present sulfur-dioxide plant would be unnecessary, and a further saving would thereby be made in the operation costs.

The method of using sulfur dioxide to control the electrochemistry of the process hardly appears to have been successful. By this method, only two-thirds of the copper in solution could be deposited by electrolysis, and that part with a current efficiency of only 62.9 per cent. If, in removing the foul effects of a solution, it is necessary as a last resort to discard any part of the solution, the method employed can never be wholly successful chemically, or economical. The chemistry should control the process, instead of the process controlling the chemistry. The New Cornelia Copper Co.'s process, when controlled as described, would still have the objection that it is not self-contained. It depends on an outside chemical plant for its supply of sulfuric acid. In some localities this is a very expensive and objectionable feature and confines this kind of process to oxidized ores and to localities where sulfuric-acid can be obtained at reasonable cost.

An electrochemical process for the treatment of copper ores should be self-contained without acid works, and should be capable of treating any class of copper ore (except those carrying metallic copper) by producing the solvent from the ore itself in the process by roasting the ore in the presence of sulfur. The ores of the Ajo mine are ideal for this method of treatment. By mixing the sulfide ores with the oxidized ores and roasting the mixture, the acid required for the solvent would be produced, even if the ores or mixture contained very little sulfur.

The writer has made exhaustive experiments in the treatment of ores from the Ray and Inspiration mines in Arizona and from many others. The results of these show that any of these siliceous ores or mixtures of these ores carrying as low as 1 per cent. sulfur for each 2 per cent. copper, when roasted under proper conditions, will produce sulfuric acid sufficient to extract 90 per cent. of the copper in the ore. This method of treatment also controls the chemistry of the problem, as the iron is oxidized to such an extent that the soluble iron in the ore will be reduced so that it will average not more than 0.10 per cent. and the other impurities are controlled at the beginning. The writer has found, in treating the very rich copper ores of the Katanga district of the Belgian Congo by this method, that ores carrying as high as 22 per cent. copper required to be roasted with only 4 per cent. sulfur in the form of iron pyrite to produce the required acid, or a proportion of 1 per cent. sulfur to 5.50 per cent. copper.

In this method, the ore is crushed to the proper fineness, which will depend on the character of the ore but in any case not coarser than will pass ¼-in. mesh screen. If the ore contains no sulfur, sulfur can be added in any form, preferably as sulfide ores or iron pyrite crushed a little

finer than the ore, so that the mixture will carry not less than 1 per cent. sulfur in siliceous ores carrying 1 to 2 per cent. copper. For ores carrying a greater content of copper, the sulfur can be less than this proportion. The ore or mixture is then roasted in any of the common circular multiple-hearth mechanical furnaces, such as the Wedge or MacDougall type, properly controlled so that part of the copper in the ore will combine as $CuSO_4$ and part as CuO. The copper combining as $CuSO_4$, in roasting, furnishes the acid required to extract the copper combined as CuO when decomposed by electrolysis.

The ore, when roasted, is leached first (in starting a plant) with water until the copper combined as $CuSO_4$ is leached from the ore. When this water leach contains about 3 per cent. copper it is electrolyzed and about 1.25 per cent. copper is precipitated leaving about 1.75 per cent. copper and forming about 1.93 per cent. free acid in the solution. This acid solution is then used as a solvent for the CuO in the ore and continuously passes in a circuit through the ore on the one side and the electrolysis on the other until all the soluble copper is extracted from the ore and precipitated as electrolytic copper.

The acid consumption is reduced to the minimum by preparing the ore by roasting in the presence of sulfur, because, in the first place, in roasting, part of the copper in the ore combines as $CuSO_4$, which is soluble in water, and, in the second place, the base elements become practically insoluble in the weak acid formed in the process, and there is no acid required over what is regenerated in the process. The result of an extended research on this subject by the writer shows that ores carrying about 2 per cent. copper and over 60 per cent. silica and not over 1 per cent. lime, require about 0.65 per cent. copper in the roasted ore combined as $CuSO_4$, or the equivalent, when decomposed, of about 1 per cent. free H_2SO_4, to maintain the acid in the plant without loss. This equals an acid consumption of about 20 lb. of 100 per cent. H_2SO_4 per ton of ore treated. By this method, the metallurgy of copper is greatly simplified; all classes of copper ore (except ores carrying metallic copper) can be treated successfully and economically, a high extraction of the copper can be made, and refined copper produced, without chemical works, fine crushing, concentration, smelting or refining.

DISCUSSION

W. L. AUSTIN, Riverside, Calif. (written discussion).—The profession is much indebted to the management of the New Cornelia Copper Co. for releasing the valuable data contained in the paper by Messrs. Tobelmann and Potter. While there must have been good reasons for the procedures adopted, in view of the results obtained the question arises as to whether the methods employed are the very best that might be used.

According to the figures given for 1918, there were passed through the electrolytic vats, in round numbers, an average of 8950 tons of solution in 24 hr., from which about 13 per cent. of the contained copper was extracted; afterwards the solution, still carrying .87 per cent. of the original copper content, was returned to the ore-leaching department to recommence the cycle. In other words, the electrolytic method is shown to extract a relatively small percentage of the copper contained in the electrolyte while necessitating the circulation of a large tonnage of solution for the sole purpose of picking up a little more copper before returning to the electrolytic vats. Because of carrying this load of copper around and around through the whole treatment system, which serves no useful purpose, the idea forcefully suggests itself, Would it not be better practice to remove the copper wholly from the lixiviant by some chemical precipitant—hydrogen sulfide for instance—which releases the solvent in condition to go back to the ore vats? Copper precipitated in the form of sulfide generally contains 60 odd per cent. of metal and is, therefore, sufficiently concentrated to be handled in any one of several ways with which metallurgists are familiar.

The use of hydrogen sulfide for metallurgical purposes is no novelty, but the knowledge gained in its application appears to have been temporarily overlooked. It will be recalled that there are a number of methods for producing the gas to choose from, one or the other of which will generally meet local conditions. Those who have investigated the application of the reagent to metallurgical purposes find it replete with interesting possibilities. In any event its use in copper leaching operations suggests one way of avoiding sending 87 per cent. of the copper already extracted from an ore back into the cycle of operations. It also simplifies the removal of copper from discarded solutions.

That there is room for improvement in leaching processes, as now applied to copper ores, is further evidenced by information contained in the latest annual report of the Utah Copper Co. The operation of the leaching plant of that company is said to have been hampered by an inadequate precipitating and drying system which reduced the rated capacity (3000 tons daily) two thirds. The cost of the copper produced "crediting an allowance for copper in stock solutions, and adding smelting and selling charges" is given as 15.1 c. per lb., with apparently no charge made for mining. If a charge of 45 c. per ton for mining is added the cost of the copper would be increased to 19.3 c. per lb. The leaching plant was closed Jan. 1, 1919, the first department to experience curtailment. Extraction of copper from ore by the use of aqueous solutions has attained a fairly satisfactory stage of development, but the methods in use for removal of the metal from the lixiviant, and its subsequent treatment, can be much improved in some instances.

Reverberatory Furnace for Treating Converter Slag at Anaconda

By Frederick Laist* and H. J. Maguire,† Anaconda, Mont.

(New York Meeting, February, 1920)

The ore from the Butte mines of the Anaconda company is quite siliceous; that is, it contains considerably less iron than is needed for the fluxing of the silica. The direct smelting of this ore, therefore, requires the addition of considerable fluxing material. The only flux available in sufficient quantity at Anaconda is limestone containing no metallic minerals. This necessarily makes the direct smelting of the ore so expensive that it is more profitable to subject the ore to a preliminary treatment by concentration. However, as the losses in the concentrator were very high, compared with the losses in the blast furnaces, it was found, by calculation, more profitable to send ores containing more than a given percentage of copper to the blast furnaces, in spite of the higher costs of treatment. The dividing point was dependent on various factors, the chief of which was the prevailing market price of copper. It was customary, therefore, to segregate the ore as mined into two classes. Ore in the first class generally contained 5 per cent. or over of copper; this was sent directly to the blast-furnace department. Second-class ore contained less than 5 per cent. of copper, and averaged around 3 per cent.; it went to the concentrating department.

With the introduction of the flotation process, it was found possible to maintain an average recovery, as concentrates, of 96 per cent. At the same time, the cost of reverberatory smelting was very materially decreased by the use of pulverized coal. These two changes in practice made the blast furnaces unable to compete with the reverberatory furnaces on a cost basis. The distinction between first- and second-class ore was therefore abandoned, and the ore was treated by concentration.

Obviously, on ores as high in iron as the Butte ores, the concentrator produces a product that is self-fluxing; in fact, it is possible to produce a concentrate containing more iron than is necessary to flux the silica. Under these conditions, the amount of basic fluxing materials required for the smelting operations became very small and the converter slag lost its former value as a blast-furnace flux. For this reason, a less expensive method of recovering the copper, silver, and gold contained in it than smelting in blast furnaces had to be found. It was not feasible

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to pour the slag into the regular reverberatory smelting furnaces because these were located in a building a considerable distance from the converter building and on a higher level. It was, therefore, decided to undertake some investigations to determine whether the converter slag could be treated in a single large reverberatory furnace, which would be constructed for this special purpose in one end of the converter building.

It seemed that the successful treatment of the converter slag would require the reduction of Fe_3O_4 contained therein to FeO. Silica would have to be furnished to combine with the FeO so as to produce a slag containing not less than 30 per cent. silica. At the same time, iron sulfide would have to be furnished to combine with the particles of metallic copper and white metal and carry them into a comparatively low-grade matte. All of these reactions, it was thought, could be brought about by the addition of unroasted or partly roasted fine concentrates and fine siliceous ore. The experiments were carried out under the supervision of F. F. Frick, research engineer for the Anaconda company, and gave reasonably satisfactory results.

Data on Experimental Furnace Apparatus and Operation[1]

A small reverberatory furnace with a hearth area of 32 sq. ft. (4 ft. by 8 ft.) was used. About 350 gal. per day of fuel oil was used for firing. A mixture of cold converter slag and cleanings was charged and melted, then the sulfide materials and fluxes were added and melted. A shortage in the supply of fuel oil necessitated shutting down the furnace sooner than was desirable, but the data obtained were sufficiently satisfactory to pronounce the method successful. The data indicated that the desired results can be obtained by using first-class ore screenings to the extent of 25 to 50 per cent. of the weight of converter slag together with some fine concentrate to hold down the tenor of the matte.

The work was divided into five periods, each period covering the time a certain class of material was used with converter slag: (1) First-class ore screenings; (2) fine concentrates; (3) calcine; (4) first-class ore screenings; (5) converter slag with no additions.

Period	1	2	3	4	5
Average tons per 24 hr	1.64	1.59	3.0	2.11	1.44
Average per cent. copper in slag	0.34	0.65	0.60	0.77	0.83

Charge

Period	1	2	3	4	5
Converter slag, pounds	300	200		200.0	200
Dirty converter slag, pounds		100		100.0	100
Screenings, pounds	150			75.0	
Round-table concentrate, pounds		150			
Lime rock, pounds	45	45		37.5	
Calcine, pounds			300		
Total	495	495	300	412.5	300

[1] Extracted from Research Department Report of 1915.

PRODUCTS ANALYSIS

Slag

PERIOD	1	2	3	4	5
CaO, per cent	6.60	6.30	4.2	6.00	3.90
Copper, per cent	0.34	0.65	0.6	0.77	0.83
SiO_2, per cent	40.00	38.70	37.8	37.80	39.90
FeO, per cent	41.10	40.50	44.3	45.00	44.30

Matte

PERIOD	1	2	3	4	5
Copper, per cent	20.0	40.0	44.0	50.0	48.0

CHARGE ANALYSIS

	Clean Converter Slag				*Dirty Converter Slag*		
PERIOD	1	2	4	5	2	4	5
Copper, per cent	1.91	1.86	2.60	1.96	4.63	7.8	7.9
SiO_2, per cent	22.6	23.0	22.5	23.3	28.8	24.5	25.2
FeO, per cent	65.7	62.7	63.0	64.6	51.4	54.4	53.2

	Screenings		*Fine Concentrates*	*Calcine*
PERIOD	1	4	2	3
Copper, per cent	6.54	6.5	9.07	8.8
SiO_2, per cent	46.2	46.0	38.9	25.1
FeO, per cent	18.6	19.6	17.5	42.3
CaO, per cent				1.3
S, per cent	19.0	18.4	19.1	9.9

There were 20 charges in the first and second periods, 16 charges in the third, 13 charges in the fourth, and 9 charges in the fifth.

Copper concentrate with a high sulfur content mixed with converter slag in the furnace gives the result desired when thorough contact is effected. The reaction that probably occurs when concentrate is mixed with slag is $2Fe_3O_4 + S \rightarrow 6FeO + SO_2$. The completeness of such reaction depends on the intimate contact of the concentrate with the hot liquid converter slag, on which also depends the quality of the resultant waste slag.

FURNACE AND EQUIPMENT

On the basis of these results, it was decided to construct a large furnace. The location, while not ideal, was the most convenient and has proved to be well adapted to requirements. The inside length of the

furnace, from burners to skimming block, is 153 ft. (46 m.) and the inside width is 23 ft. 4 in. (7.1 m.). It has a flue connection 8 ft. 6 in. by 6 ft. (2.5 by 1.8 m.) which leads to a brick-lined 12-ft. (3.6 m.) steel stack 200 ft. (60.9 m.) high. Two Stirling boilers, type *M*, with a rated capacity of 865 hp. each, are placed in the flue to convert waste heat from the gases into steam. The flue is split into two compartments and a boiler is placed in each so that either or both boilers can be used at the same time. A section of each flue immediately in front of the boilers is 15 by 13 ft. (4.5 by 3.9 m.). The furnace is equipped with hoppers on both sides for

FIG. 1.—POURING HOT CONVERTER SLAG INTO SLAG FURNACE FOR TREATMENT; SLAG IS TRANSFERRED IN LARGE LADLES BY 60-TON OVERHEAD CRANES.

the full length of the furnace and in the center for 100 ft. from the burners. The hoppers are kept supplied, by the local tramway system, with materials as needed. Charging tunnels were provided so that all dumping of calcine or other dry material may be accomplished with the least hardship to the operators. A fan maintains a suction in the tunnels.

Pulverized coal is conveyed by a 14-in. (35.5-cm.) screw conveyor from the coal-dust plant a distance of 525 ft. (160 m.) and is delivered to a 24-ton bin back of the burners. Five coal burners are used. Air is supplied by a General Electric compressor driven by a direct-connected 75-hp. motor running at 3600 r.p.m. The air is maintained at a pressure of 16 ounces.

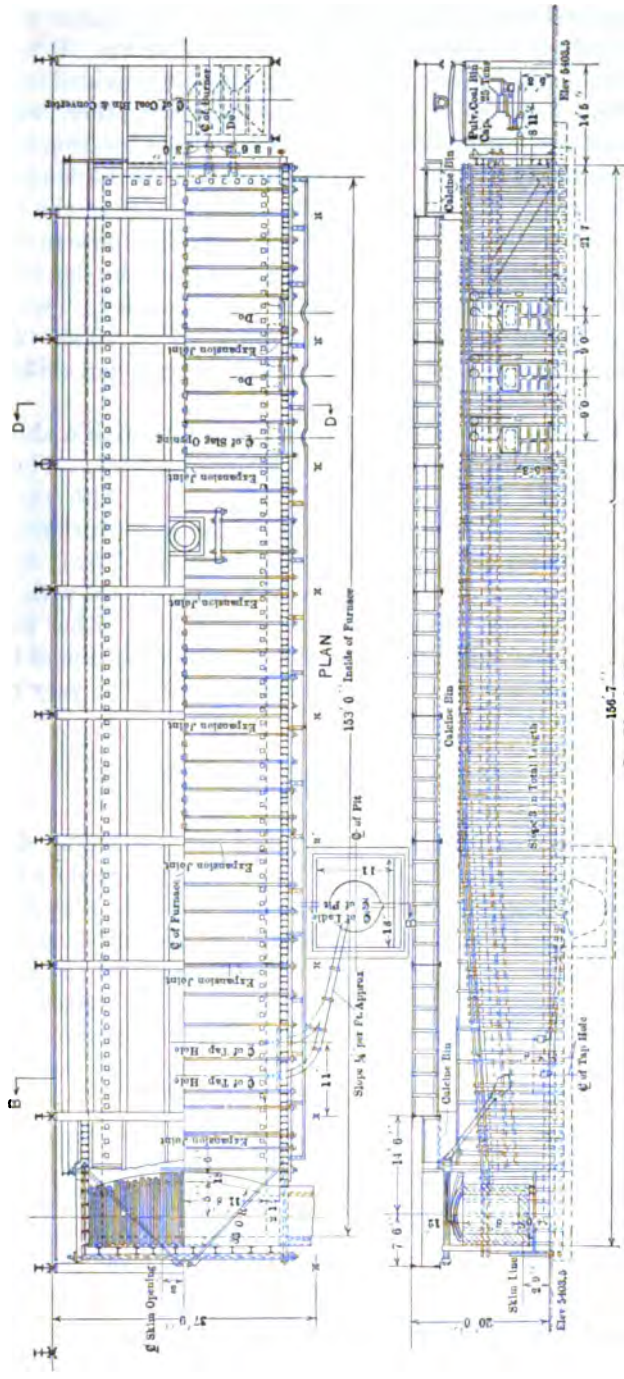

FIG. 2.—SLAG FURNACE FOR CONVERTER SLAG.

The slag is poured into a slag-charging device which consists of a cast-iron launder placed on wheels and having a replaceable lip. It is shown in Fig. 1. Three openings in the side of the furnace are provided to accommodate this spout, any one of which can be used, the other two being bricked up. They are just under the skewback. Their location is shown in Fig. 2. Immediately over the slag-charging spout is the hopper containing the concentrate; the hopper on the opposite side of the furnace also contains concentrate. From this point back to the burners the hoppers carry specially prepared calcine. All hoppers from the slag-charging spout forward carry siliceous material for protecting the sides. Two charge hoppers in the center of the furnace are equipped with 10-in. (25-cm.) openings so that cold material, such as matte or slag when chilled, can be fed directly.

The skimming block is water-cooled and connects with a short slag launder, also water-cooled, and is lined with magnesite brick. The waste slag flows continuously and is granulated with water. The top of the skimming block is 18 in. (45.7 cm.) above the bottom of the furnace. The matte "tap hole" plates are set in a water-jacket about 5 ft. (1.5 m.) on centers; they are made of cast iron 13 in. (3.9 cm.) square with a 2-in. (5-cm.) hole in the center. Matte can be tapped from either tap hole to the matte ladle in the ladle pit. The difference in elevation of the tap hole in each plate is 8 in. (20 cm.) so that it is possible to vary greatly the amount of matte in the furnace.

Operation of Furnace

The capacity of this furnace for treating converter slag depends somewhat on the character of the slag. It is necessary to strike a balance between a high-silica slag from converters, which would be very desirable for the slag furnace, and a slag that would give the greatest length of life to the converter lining. A slag carrying from 21 per cent. to 23 per cent. SiO_2 meets these requirements very well. As much as 783 tons of slag have been charged into the furnace in 24 hr. The calcine, concentrate, and tailing (siliceous material) added to the furnace that day made a total of 1228 tons. This is a larger tonnage than is desirable.

The converter slag is charged to the furnace as it comes from the converters, in ladles which carry about 9 tons of slag. Some care is required to regulate the charging of the slag and an attempt is made to charge not over four ladles an hour. Some ladles may remain on the floor from 20 to 30 min. before the furnace can receive the slag, so as to avoid rushing the material through the furnace. As the slag is charged, a small stream of fine concentrate is dropped into the furnace just over the inflowing slag. This is the only mixing that occurs with slag and concentrate.

A specially prepared calcine is smelted on each side of the furnace from the slag-charging spout to the back of the furnace. The molten material from this mixes also with the converter slag. This furnishes the bulk of the silica for the final slag and sulfur for the matte. Additional silica, however, is taken up from the tailings, or siliceous material, along the side of the furnace toward the front. Matte is tapped from the side

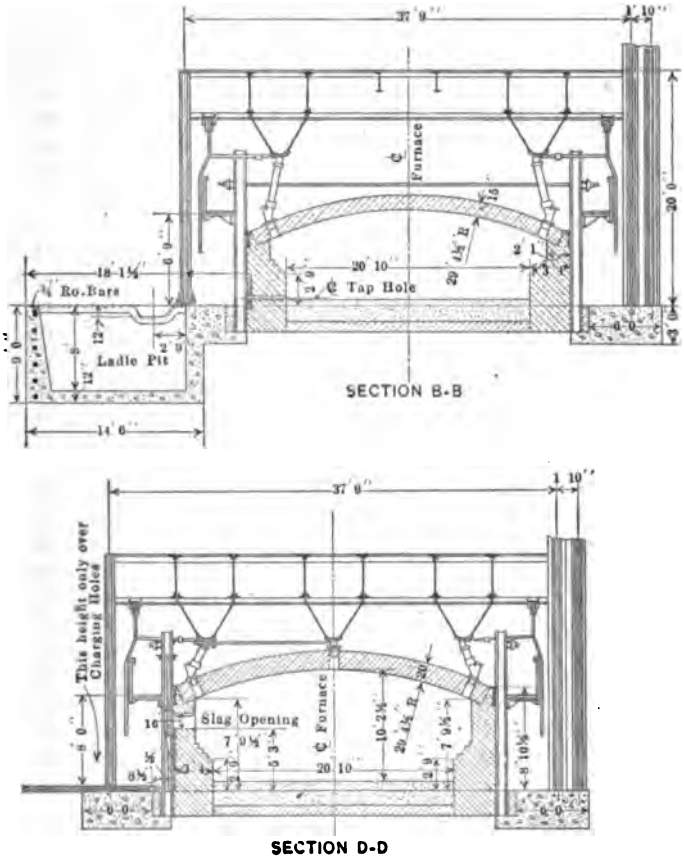

FIG. 3.—CROSS-SECTIONS THROUGH SLAG FURNACE.

of the furnace, about 25 ft. from the front, to the standard ladle used in the converter plant, which holds about 10 tons. This matte is tapped as required by the converters. The slag from the furnace flows continuously and is granulated with water and carried to the dump, see Fig. 4.

RESULTS OBTAINED

The results for July, 1918, are given here, as being those of a typical month.

Tons of Material to Converter Slag Furnace

Date	Converter Slag	Copper Concentrate	Special Calcine	Old Works Tailings	Total Tons	Coal Burned	Coal Ratio Whole Charge	Coal Ratio Cold
1	783	77.3	352.7	14.7	1,227.7	73	16.81	
2	527	58.8	368.7		954.5	79	12.08	
3	617	38.5	361.6	19.6	1,036.7	75	13.82	
4	603	87.4	392.1	19.4	1,101.9	75	14.69	
5	536	54.0	370.6	35.8	996.4	78	12.77	
6	554	78.3	340.2	13.3	985.8	77	12.80	
7	490	63.1	343.5	15.6	912.2	78	11.69	
8	571	69.0	326.8	16.8	983.6	77	12.77	
9	531	61.0	367.6	17.3	976.9	78	12.53	
10	517	46.2	354.2	26.0	943.4	75	12.58	
11	499	51.7	396.0	18.0	964.7	71	13.59	
12	567	57.5	331.7	12.2	968.4	68	14.24	
13	522	63.0	368.7	17.0	970.7	75	12.94	
14	621	59.0	403.4	13.4	1,096.8	76	14.43	
15	454	57.3	325.7	15.8	852.8	81	10.53	
16	643	56.0	377.6	18.2	1,094.8	61	17.95	
17	585	61.4	382.3	13.6	1,042.3	83	12.56	
18	486	46.9	371.0	17.4	921.3	83	11.10	
19	531	56.5	374.7	20.6	982.8	81	12.13	
20	498	47.0	357.9	27.5	930.4	83	11.21	
21	558	74.5	418.3	9.8	1,060.6	83	12.77	
22	473	50.5	418.5	19.4	961.4	83	11.58	
23	522	76.0	398.5	17.9	1,014.4	82	12.37	
24	437	46.2	354.0	37.5	874.7	87	10.05	
25	549	53.9	392.6	20.9	1,016.4	81	12.55	
26	509	44.5	391.2	21.4	966.1	87	11.10	
27	581	47.6	373.7	26.0	1,028.3	87	11.82	
28	581	38.8	410.4	31.6	1,061.8	86	12.34	
29	468	39.7	432.0	15.5	955.2	82	11.65	
30	545	37.7	436.5	22.0	1,041.2	82	12.70	
31	455	49.0	388.4	21.5	913.9	79	11.57	
Total, dry...	16,813	1,748.3	11,681.1	595.7	30,838.1	2436		
Daily average.....	542	56.4	376.8	19.2	994.7	78.6	12.66	5.76

PER CENT., BY WEIGHT, OF MATERIAL TREATED

	PER CENT.
Converter slag, 16,813 tons	54.5
Concentrate, 1,748 tons	5.7
Calcine, 11,681.1 tons	37.9
Tailings, 595.7 tons	1.9
Total	100.0

Copper in all material treated, pounds	3,459,448
Copper in all converter slag, pounds	1,328,227
Copper in all other material, pounds	2,131,221
Silica to slag, pounds	17,232,647
Slag produced, tons	25,268
Copper in slag, pounds	277,948

Recovery of copper based on silica balance, 91.97 per cent.

Analyses of Converter Slag Furnace Charge

Date	Converter Slag, Per Cent.		Special Calcine, Per Cent.					
	SiO_2	Cu	Cu	SiO_2	FeO	S	CaO	Al_2O_3
1	23.5	3.9	8.1	28.0	39.7	10.1	3.1	
2	22.1	3.9	7.3	38.0	34.8	9.7	1.2	
3	22.7	3.4	8.3	34.2	34.1	7.2	2.2	
4								
5	23.5	2.7	7.5	33.8	35.5	9.7	2.4	
6	23.7	2.7	7.5	37.2	33.8	9.9	2.0	
7	24.0	2.9	7.9	36.8	35.2	7.7	1.8	
8	22.5	2.7	7.9	35.4	35.6	9.0	2.3	
9	22.4	2.9	8.0	35.8	35.7	9.1	1.0	
10	22.9	3.1	8.0	36.4	35.5	9.4	1.5	
11	24.0	3.4	7.3	31.8	32.5	7.6	5.7	
12	22.7	3.2	7.2	38.6	24.3	7.5	2.7	
13	22.5	4.0	7.2	30.8	37.5	8.9	3.1	
14	22.4	3.4	7.8	31.8	37.1	6.5	3.9	
15	22.7	3.3	7.4	31.6	36.7	7.1	3.8	
16	23.1	3.2	6.8	31.6	34.7	8.2	3.9	
17	22.5	2.9	7.0	35.0	34.7	7.5	3.4	
18	21.3	3.9	7.4	31.0	35.9	8.9	4.6	
19	21.3	3.7	7.1	31.8	36.7	8.8	3.6	
20	20.7	3.4	7.2	31.4	38.5	9.9	3.8	
21	21.3	3.7	7.4	30.4	38.6	8.8	3.8	
22	23.7	3.1	6.9	31.0	36.6	9.3	3.8	
23	23.1	3.2	7.5	31.8	38.0	9.7	3.0	
24	21.2	3.7	6.8	35.4	35.0	6.8	2.8	
25	22.2	3.5	6.9	34.2	35.2	8.3	3.0	
26	21.0	3.9	6.7	33.2	35.4	9.2	2.6	
27	22.3	3.0	7.4	32.8	37.2	8.8	3.0	
28	22.8	2.9	6.7	35.0	34.8	8.0	3.0	
29	23.9	3.2	7.1	31.2	36.5	8.6	3.8	
30	22.5	3.0	7.1	33.8	35.6	10.7	2.5	
31	23.1	3.2	6.6	31.5	35.2	14.0	2.7	
Monthly assay	23.3	3.95	7.85	30.8	36.3	8.8	3.3	5.9
Converter slag			3.95	23.3	61.2	0.8	0.1	5.9
Old-works tailings			2.10	80.0	5.2	3.4	0.2	6.5
Concentrate			7.64	19.2	37.9	35.6	0.1	4.2

Analyses of Converter Slag Furnace Products

Date	Slag, Per Cent.				Matte Per Cent.
	SiO_2	FeO	CaO	Cu	Cu
1	31.0	55.0	1.2	0.61	51.4
2	29.4	54.2	1.2	0.66	43.5
3	30.6	52.5	1.2	0.59	38.7
4					
5	33.8	49.6	1.6	0.48	37.9
6	35.2	49.2	1.1	0.48	36.6
7	35.0	49.7	0.9	0.48	40.0
8	34.0	51.8	0.9	0.54	37.3
9	33.0	51.7	1.1	0.52	39.7
10	35.4	49.1	1.2	0.45	40.4
11	34.4	49.3	1.5	0.51	50.8
12	33.6	51.5	1.2	0.49	44.9
13	32.0	51.8	1.8	0.51	42.2
14	31.8	53.2	1.5	0.60	41.9
15	32.0	52.6	2.1	0.59	42.4
16	31.8	53.0	1.8	0.59	40.8
17	32.0	53.1	1.7	0.49	39.9
18	32.0	53.0	2.5	0.52	41.2
19	31.4	53.0	2.0	0.60	40.5
20	32.0	53.5	2.2	0.54	39.7
21	33.0	51.5	2.2	0.50	37.2
22	33.2	52.8	2.5	0.44	34.8
23	33.0	52.2	2.3	0.47	34.2
24	32.2	52.0	2.0	0.48	37.0
25	32.8	51.5	1.7	0.47	39.4
26	33.4	51.5	1.7	0.50	42.1
27	31.6	51.7	2.1	0.54	40.9
28	31.4	53.0	1.7	0.56	44.1
29	33.6	51.0	1.7	0.50	42.2
30	32.6	51.7	1.5	0.51	42.4
31	33.0	51.7	1.9	0.50	36.6
Monthly assay....	34.1	53.3	1.7	0.55	40.6

The average cost for treating converter slag during the year 1918, after segregating the cost of all other material and assuming this other material to have pursued its regular course through the smelter, was $0.6126 per ton. The cost per ton for the second six months of 1918 was $0.4648. There were no repairs made to the furnace during these last six months. This accounts partly for the lower cost, but there was a difference also in the tonnage of converter slag handled. During the first six months, 78,153 tons of converter slag were treated while 93,587 tons were

C. G. MAIER, New York, N. Y.—I think, as far as the last question is concerned, regarding the magnetite in the final slag, one normally would not expect to have much difference between the magnetite of this slag and that which would usually be obtained in reverberatory practice, which magnetite would average between 3 and 5 per cent. The fact that at Anaconda they get the copper out of the converter slag indicates that any original magnetite greater than that percentage has probably been reduced.

E. E. THUM, New York, N. Y.—I might call attention to the fact that C. G. Maier and G. D. Van Arsdale, over a year ago, published some very interesting facts[2] on the way in which copper was held in slag. From a perusal of those results, it seemed to me that their conclusions could be summarized as follows:

Copper is held in furnace slags to a certain small extent as a true solution of sulfide, while the balance occurs as globules of white metal floated by attached gas bubbles. Continued settling would not appear to reduce the quantity of the latter, which could only be done by changing the composition of the slag so as to practically eliminate the occurrence of ferric oxide. Converter slags may contain as high as 0.5 per cent. of copper in true solution, with the remainder present as particles of white metal, yet as the blow continues the soluble copper continually decreases. Here is evidence that practically no copper silicates are formed in normal furnace practice. The microscopic and analytic work of Messrs. Maier and Van Arsdale was keenly worked out and no exception could be taken to their conclusions.

I would like to see Mr. Laist, and his staff at Anaconda, present data that will correlate the work they have done on a large industrial scale to the work the Phelps-Dodge men have done in their laboratory research. It would also be interesting to know whether Mr. Maier has been able to reduce the copper content of his furnace slags by an application of the information he has so generously published.

C. G. MAIER.—Since making the investigation of which Mr. Thum speaks, we have done quite a lot of work that has not been published (it may possibly be) concerning the reduction of magnetite when it is normally added to ordinary reverberatory practice, that is, specifically by the addition of converter slag to the usual type of reverberatory as operating in the plant. We find that, under those circumstances, a more or less general reduction of magnetite is always obtained. This reduction varies with circumstances and depends on the firing, the grade of matte made, and so forth. But I cannot say that the work which the Phelps-Dodge Corpn. did along these lines has been done on any large, practical

[2] *Eng. & Min. Jnl.* (May 10, 1919) **107**, 815.

scale, except to the extent that we have made microscopic examinations of typical reverberatory slags as they come from a furnace, to which the converter slag has been added. Under those circumstances, there is no doubt that there is reduction, and you have to get that reduction in order to best get the copper. I hope that we will be able soon to publish results showing what actually occurs because of such addition.

E. H. ROBIE, New York, N. Y.—Have they done any work at Anaconda with settling converter slags in blast-furnace settlers?

CHAIRMAN MATHEWSON.—Not at Anaconda, but it was tried at some of the other plants in which the Anaconda Company was interested—Tooele, for instance.

E. H. ROBIE.—That is the way the converter slag at the International Nickel Co. Smelter is settled. Formerly, they poured the molten slag into the reverberatory, but the slag loss was so high that this had to be discontinued. For some time they then poured it out on the dump, broke it by hand, and charged it in solid form into the blast furnaces; later it was found much more economical to pour it into the blast-furnace settlers. With the very low-grade matte made there, sometimes as low as 15 per cent. (ordinarily about 22 or 23 per cent.), they found the slag loss increased very little by pouring all the converter slag back into the settlers, and with such a low grade of matte, there was a great deal of converter slag. The recovery was extremely hard to figure out, but it was estimated at about 80 per cent.; that is, it was assumed that about 80 per cent. of the combined copper-nickel in the converter slag was obtained in the blast-furnace matte.

E. E. THUM.—It seems to me quite essential, for the advancement of copper metallurgy, that some questions such as Mr. Van Arsdale and Mr. Maier are working upon should be settled. Anyone traveling through the Western copper smelters immediately notices the general similarity in most of their machinery and methods, doubtless as a result of the strong influence a few men, such as the chairman, Mr. Mathewson, have had upon the revolution in practice occurring since most of us started work. All the more noticeable, therefore, are the various practices in use for handling converter slag. Each man has a different idea about the proper way of taking care of converter slag, and each one has pretty good experience to fall back upon in support of his opinion, at least, he considers it good. Since, as Mr. Robie pointed out, there is a tremendous quantity of the stuff being made all the time, some rationale should be developed which would allow a person to decide intelligently how to dispose of it.

Probably based on the idea, implied if not admitted, that the copper in these slags is held in complex compounds that cannot be broken up in the approximately neutral reverberatory furnace, many plants allow the

slag to solidify and resmelt it in a blast furnace. The slag-casting machine may be a series of stationary or tilting pans, a chain of molds traveling in a straight line or about a "merry-go-round," or the slag may be poured out in a thin layer on an orebed, or even into a sump or a hole in the ground to be reclaimed later by steam shovel or grab bucket.

If the plant possesses no blast furnaces, or the management is willing to brave slag loss to save coke, the slag is charged into reverberatories. Here, again, considerable variation is noted; cars may be switched to the charging track and the liquid slag poured through the furnace roof with the maximum fall possible; pots may be poured by cranes into slag launders delivering the slag through the side or back wall at a moderate head, or cold skulls may be used for "manger" filling.

Accepting Maier and Van Arsdale's conclusions that Fe_3O_4 in slag oxidizes iron sulfide at the surface of suspended matte particles, forming little ballons of SO_2 gas, one readily sees the truth of the contention advanced by Heggie and his El Paso associates. There the statement was made to the speaker that in a reverberatory furnace a low-iron slag will be low in copper, whether or not converter slag is charged. Unfortunately, the ore supply of a smelter is likely to be such that a low-iron slag is commercially impossible; evidently, in this case, more attention to the state of oxidation of the slag would be important. Green's practice at Hayden, of dropping converter slag from a maximum height sheer into a furnace bath, is rational on the basis of washing out the values by actual contact with the underlying matte. At any rate, a mere settlement for liquation, either in a ladle or forehearth, appears to be useless.

CHAIRMAN MATHEWSON.—The point taken by Mr. Thum is a good one and I think all those interested in actual smelting operations should add their quota to the knowledge we are gradually accumulating in the Transactions of the Institute, not only in papers, but in discussions on these points. These little things mean a great deal, but they are overlooked in too many instances. The diversity of practice in this one matter is common knowledge to metallurgists, and there should be a good reason for the diversity, or a more standard practice should be adopted.

W. C. SMITH.—Soon after the paper by Mr. Van Arsdale and Mr. Maier was published, a discussion arose concerning the pouring of converter slag into the settlers, and the so-called settling or washing. As a result, we examined several slags sent us by the Tennessee Copper Co. One of these was the slag from a furnace treating green ore, one was from the matte-concentrating furnace, one was from converter slag, and one was taken from the settler overflow after the converter slag had been poured into the settler.

When examined under the microscope, the slag from the raw ore showed practically no magnetite; the slag from the matte-concentrating furnace showed some slight evidences of magnetite; the converter slag was loaded with it; the slag from the settler, into which the converter slag had been poured, was quite well loaded with magnetite. It appeared that the magnetite in the converter slag had not been reduced, but simply diluted with a large amount of blast-furnace slag.

We did not examine the slags for copper, so that we cannot say anything about that. Very recently, we ran several successive charges of straight converter slag in a blast furnace and then took samples from the spout, about the time, or shortly before, the converter slag was due at the spout, and at intervals of 15 min. until we knew the converter slag had gone through the furnace. We ran rather a high coke on the charge, from 12 to 14 per cent., and none of our slag samples showed any marked evidence of magnetite.

C. G. MAIER.—The reason why there is suspension of copper in slags is that there are oxidizing conditions which, acting on iron or copper sulfide, produce sulfur dioxide, causing the metal containing pellets in the slag to be floated. The only way to get rid of the suspension reaction is to reduce the magnetite.

Volatilization in Assaying*

By Frederic P. Dewey,† Washington, D. C.

(New York Meeting, February, 1920)

It is common to blame irregular assay results upon volatilization and much has been written upon the subject, but there is no real evidence that, in a properly conducted assay, the loss of either gold or silver by volatilization is sufficient to affect appreciably the result, even when arsenic or antimony may be present. Bulk assays of flue dust from assay muffles have been published, but the data given are totally insufficient to even approximate the volatilization from a single assay; and such figures as we have indicate the volatilization to be extremely small. Diligent search in the literature and wide inquiry among assayers and instructors have failed to produce a single case where the litharge volatilized in making an assay has been collected and assayed for gold and silver. Having attempted to do this, with most indifferent success, I am not surprised that this has not been done.

While various textbooks give volatilization as a cause of loss in cupellation, it may safely be said that in the rare cases where this volatilization is sufficient to affect appreciably the result it is due to excessive temperature. Percy[1] says "The loss of silver by volatilization during cupellation is very slight (unless the temperature has been much too high), and may be disregarded." This statement is repeated by the Beringers[2] and Smith,[3] who includes gold with silver. Mitchell[4] says the litharge fume rarely contains over one ten-thousandth of silver. Campredon[5] says that at a proper temperature no silver is lost by volatilization.

Primarily, excessive temperature may be due to too high general temperature in the muffle; but it may often be due to temperature localized within the bead by oxidation of the metals and this may be influenced by other causes than the general temperature. I have shown an ex-

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* Published by permission of the Director of the Mint.

† Assayer, Bureau of the Mint.

[1] John Percy: "Metallurgy—Silver and Gold." Pt I, 249. London, 1880.

[2] C. and J. J. Beringer: "Text-book of Assaying," 101. London, 1908.

[3] Alfred E. Smith: "Sampling and Assay of Precious Metals," 170. London, 1913.

[4] John Mitchell: "Manual of Practical Assaying," 484. N. Y., 1872.

[5] L. Campredon: "Guide Pratique du Chimiste Métallurgiste et de l'Essayeur," 305. Paris, 1909.

treme case of local temperature,[6] resulting in the burning of zinc with its characteristic flame and variations in bead temperatures with uniform pyrometer readings. Volatilization from a bath of mixed metals is not the simple question of vapor pressures of the contained metals. Based entirely upon vapor pressures, Richards,[7] in speaking of the distillation of zinc from Parkes crust, says "Successively larger amounts of lead, silver, and gold come over the higher the temperature," but I have shown[8] that more silver goes with the zinc in the early stages of the operation than later.

Volatilization in Cupeling

The possible volatilization of the precious metals in cupeling is a most complex proposition. It may be due to the vapor pressure of the individual metals, the vapor pressure of alloys or possible metallic compounds, of compounds of metals with metalloids or with non-metals, particularly oxygen. Also it is not possible to draw a sharp line between true volatilization due to vapor pressure and the drag of a volatilizing body exerted upon a less volatile associate, against which is the counter-drag, or stabilizing effect, of the non-volatile upon the more volatile, all of which are influenced by concentration and association. The temperature conditions of the cupeling beads vary constantly, which may change any or all of these conditions. The oxygen supply influences them. Even more important, perhaps, is the extent to which the surface of the metal is covered and protected by the litharge formed. At moderate heats much of the button surface is covered by the litharge and the opportunity for direct volatilization of the metals reduced. Intimately connected with this is the question of secondary volatilization, oxide of lead being volatile, oxide of silver may be dragged along, even if it is not covolatile. No one knows how much, if any, of the lead, or any other metal, present in cupel fumes volatilized before oxidation.

Rose[9] suggests that gold and copper go off as "vaporized alloy" and Mitchell[10] says silver is much more volatile when alloyed with lead. Wright[11] bessemerized silver bullion high in arsenic and the arsenious oxide produced showed about 800 oz. silver per ton. I have roasted rich arsenide ores[12] at a very low temperature and the arsenious oxide given

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[6] *Trans.* (1918) **58**, 85, 89.
[7] *Jnl.* Frank. Inst. (1919) **187**, 595.
[8] *Eng. & Min. Jnl.* (1919) **108**, 87.
[9] *Jnl.* Chem. Soc. (1893) **63**, 723.
[10] *Op. cit.*, 484.
[11] *Eng. & Min. Jnl.* (1918) **107**, 263, from *Trans.* Can. Min. Inst. (1918) 992.
[12] *Eng. & Min. Jnl.* (1919) **108**, 87.

off showed only a few ounces of silver per ton. Mitchell[13] says the litharge fume in cupeling is "produced by the vapor of lead burning in the atmosphere," but gives no data.

Again other questions of molecular physics are involved. Keller[14] has shown that gold travels into copper on prolonged heating of the alloy below its melting point. So the rate at which the precious metals withdraw into the cupeling bead must affect the drag. Gillett[15] says that on heating brass, loss of zinc depends, in part, "on the rate of diffusion of zinc from the body of the melt into the surface that is losing zinc."

Loss Through Dusting

Many statements regarding volatilization in assaying are based upon data obtained under conditions entirely different from cupeling and much that has been written fails to distinguish between volatilization and dusting, which is purely mechanical. In practical operations, losses are often ascribed to volatilization that are largely, if not entirely, due to dusting and other mechanical causes.

In modern practical work, there is now probably very little straight cupellation of lead. Where works have lead rich enough to cupel, advantage is generally taken of this to work up other high-grade products, rich ores, slimes, etc. Much of the extremely rich silver ore from Cobalt, Can., has been treated in this way. These additions, particularl yvery fine slimes, favor dusting and high silver in fume or dust collected from cupeling furnaces does not prove high volatilization. Iles[16] gives many figures on fumes and dusts from various sources. A mixed cupel fume showed 85.90 oz. silver per ton; this might indicate volatilization, but the fact that it was only 72.50 per cent. lead showed dusting, oxide of lead containing 92.83 per cent. lead.

Mr. Dieffenbach,[17] has furnished a month's record of the results from the Cottrell condensers on the cupel furnaces. The fume collected weighed 24,659 lb. and contained 9863 lb. lead, or approximately 40 per cent., indicating much dust. This is accounted for by the fact that about 70 tons of slimes were treated on the lead bath. The fume contained 5830.11 oz. silver or 0.64 per cent. of the silver charged. In view of so much mechanical dusting of rich stuff, the actual volatilization must have been very small. The slimes charged contained nearly 555,000 oz. silver. In a negative way, the figures show that there was practically

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[13] "Manual of Practical Assaying," 558. 1881.
[14] *Trans.* (1919) **60**, 698.
[15] U. S. Bureau of Mines *Bull.* 73 (1916) 125.
[16] *Sch. Mines Qr.* (1899) **20**, 397.
[17] Superintendent of the Balbach Smelting and Refining Co., Newark, N. J.

no volatilization of gold for, notwithstanding the dusting, only 12.07 oz. gold were found in the fume out of 16,855 oz. charged, of which over 13,000 oz. were in the slimes.

Condensation of Assay Muffle Fumes

Various persons have reported the finding of gold and silver in the fumes condensed in the flues of muffles, but these generally show only minute quantities of the precious metals and all lack quantitative significance. Smoot[18] says "we assayed the condensed fumes from the muffle ventilation pipe and found only a very small amount of silver and practically no gold" and "this seems to indicate, in a qualitative way, that only a negligible amount of silver is lost in the lead fume."

The best figures that I know of regarding the condensation of assay muffle fumes have been supplied by Donald M. Liddell. One muffle was used only in pig copper assays by the combination method. It carried very close to 90 oz. per ton and the residue from 1 assay-ton, after burning off the paper, was scorified with 1 assay-ton lead down to about 7 gm., which was cupeled in the same muffle. The muffle had a small forced-draft apparatus at the back and all fume passed through an iron pipe, which formed a fairly efficient condenser. This pipe was cleaned out every 6 mo., during which time about 5500 assays were made, yielding about 175 gm. of litharge. One lot of 175 gm. gave 142.7 mg. silver but not enough gold to weigh. This would roughly mean the volatilization of about 0.026 mg. silver per assay or approximately 0.03 per cent. It would seem fair to divide this between the scorification and cupeling, estimating the cupel volatilization as 0.015 per cent.

Vapor Pressure and Volatility

Johnston[19] has published a most valuable review on the vapor pressure and volatility of several high boiling-point metals, giving many references, particularly of exact scientific investigations. The ultimate object of this paper was to devise a formula for determining the approximate volatility of various metals at different temperatures. The data regarding gold, however, were too scanty for this. There is absolutely no connection between melting point, vapor pressure, and boiling point. Various metals show vapor pressure below their melting point. Tin, with a melting point of 232°, is said to boil at about 2300° while copper, with a melting point of 1083°, is said to boil about 100° above tin.

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[18] Personal letter.

[19] *Jnl. Ind. Eng. Chem.* (1917) 9, 873.

Volatility of Gold

Varied statements have been made regarding the volatility of gold. Gmelin[20] says "It exhibits a scarcely perceptible volatility at the strongest heat of a blast furnace, in the focus of a burning mirror, and in a flame fed with oxygen gas." Napier[21] appears to have been the first to make systematic tests and is often quoted, but his figures are small, about 0.1 per cent., and the time of heating long, 3 to 8 hr. Makins[22] is often quoted, but his figures are extremely small even though an extraordinary heat was used in the cupellations; there is no connection with the amount of gold operated on; he simply found 0.087 gr. of gold in 1000 gr. of flue dust. The volatility of gold before the extreme heat of the blowpipe is described in Crookes.[23]

Seamon and Parker[24] heated beads of gold, 1 to 20 mg., varying periods of time, to temperatures from 1000° to 1650°. Losses were observed only twice and were attributed to unobserved errors of manipulation. Under the conditions of a cathode-ray vacuum, on prolonged heating, Krafft and Bergfeld[25] were able to observe volatilization of gold at 1070°. Moissan[26] places the boiling point at 2530°. Mostowitch and Pletneff[27] state that in oxygen, nitrogen, carbon monoxide, and carbon dioxide at 1400°, volatilization is not appreciable but is noticeable at 1250° in hydrogen. Kern and Heimrod[28] made extensive tests on the volatility of gold and silver, obtaining some interesting results, but their conditions were quite different from cupellation. Many hours heating in contact with carbon did not volatilize silver from copper, but did volatilize gold from copper, possibly by the formation of a carbide of gold. Incidentally, their quotation from Napier is faulty. Wurtz[29] gives a review of early information.

T. K. Rose has been a prolific investigator of this subject and his books and papers contain many references. In 1893, he stated[30] that volatilization of gold begins just below 1100° and at 1250° the loss per minute was four times as great as at 1100°; the loss on a charge of 1200 oz. was figured to be 0.02 per cent. per hour; the volatilization in cupellation

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[20] Leopold Gmelin: "Handbook of Chemistry," Tr. by H. Watts, **6**, 205. London, 1852.

[21] *Jnl.* Chem. Soc. (1858) **10**, 229.

[22] *Jnl.* Chem. Soc. (1861) **13**, 98–9.

[23] "Select Methods," 443. 1886.

[24] *Bull.* Missouri Min. Club (1895) **1**, 16.

[25] *Ber.* (1905) **38**, 254.

[26] *Compt. Rend.* (1905) **141**, 977.

[27] *Jnl.* Russ Met. Soc. (1915) 410, Abs. *Met. & Eng. Chem.* (1917) **16**, 153.

[28] *Sch. Mines Qr.*, **33**, 34–64.

[29] *Eng. & Min. Jnl.* (1885) **40**, 126.

[30] *Jnl.* Chem. Soc. (1893) **62**, 714.

was insignificant. Later, he says[31] that the loss in an ordinary melting furnace is seldom over 0.01 per cent. on 1200 oz. and is influenced by temperature, metal surface exposed, and time, and is increased by air passing over the metal and by impurities. Still later,[32] he says, "True volatilization of gold is so small as to be negligible at the temperatures of industrial melting furnaces, say 1000° to 1300°. It is difficult to measure with accuracy the infinitesimal amounts volatilized at these temperatures." "Even in a strong draft the amount volatilized remains exceedingly small" provided the nature of the gas does not change. Alloys, however, may take up and eject gases with spurting, which may give globules less than 0.001 mm. in diameter, which may be carried away by even a slight draft and are difficult to recover. The first table of results, p. 4, is an excellent illustration of a fact I have often met in the literature and in my own experience with gold; that is, the effect of unrecognized conditions leading to erratic results when expecting regularity.

In a paper on accuracy in assaying, Rose[33] attempted to follow the course of the gold and gives results from which he concludes that while final loss is shown in each case it does not represent the amount volatilized with certainty, errors of five determinations being accumulated here. I would add that he determined the silver and other metals left in his cornets in a lump by a reassay, which must have been subject to all the errors of the original assay.

Hillebrand and Allen[34] give some figures upon volatilization, but they exhibit serious irregularities. On gold alone two cupel recoveries exceeded the total loss and the volatilization figure on No. 4 cupel was more than twice No. 6, two cupels behind. In series B, Table IX, 15 mg. gold, 45 mg. silver, No. 3 showed a higher figure for gold volatilization than No. 6, three cupels behind it in the furnace, and on silver No. 4 showed more than No. 6. While the total losses show considerable regularity from front to back of the furnace, the ratios between volatilization and absorption are erratic. The possibility of losing gold mechanically in decanting and washing was not provided for in the volatilization tests.

Schneider[35] attempted to determine volatilization by cupeling 450 mg. gold, 50 mg. copper, 1200 mg. silver, 4 gm. lead, recupeling the resulting bead with 4 gm. lead and repeating eight times. When properly carried out, this method might give a goox approximation, but Schneider generalized as to some of his figures and assumed that no gold went into his

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[31] *Ann. Rpt.* British Mint (1906) 60; Abs. *Eng. & Min. Jnl.* (1907) **84**, 297.
[32] Inst. Min. Met. 3/20/19, see *Eng. & Min. Jnl.* (1919) **107**, 839.
[33] *Jnl.* Chem. Soc. (1893) **63**, 700.
[34] *Bull.* 253, U. S. Geol. Survey (1905) 20, 21.
[35] *Oest. Zeit. Berg. u. Huttenwesen* (1906) **54**, 98.

nitric acid, although he assayed the ten cupels for gold and silver absorbed.

I have done considerable work in trying to arrive at a figure on volatilization of gold in cupellation by the examination of the products of the operation. No determination of volatilization depending in any way on the weight alone of a bead or cornet can be convincing. The normal bead is never pure precious metal. Cornets always carry silver and copper and often lead. Gold goes into the parting acid and into the cupel. After actually determining these items and balancing the results we get a figure, which might be called volatilization, but it is a difference figure and bears the errors, both plus and minus, of much analytical work; therefore it must be handled with judgment. Sometimes the figure indicates an appreciable loss; sometimes it gives practically a balance, indicating no loss; a gain also has been shown.

All these points are shown in one test. The San Francisco mint prepared an ingot of standard gold, 900 gold 100 copper, for test purposes. It was extremely close to 900 fine in gold. Three sets of nine assays, three rows of three, were run at three temperatures, the regular heat for this work, very low, and very high. The regular heat showed a slight loss of gold. The very low heat showed a gain. The very high heat, which should have favored volatilization of the gold, gave practically a balance, the figures showing a loss of only 0.005 mg. for the set. The figures are as follows:

	Regular Heat, Milligrams	Very Low Heat, Milligrams	Very High Heat, Milligrams
Silver in cornets	3.51	3.55	3.02
Copper in cornets	0.31	0.23	0.32
Lead in cornets	trace	trace	trace
Total in cornets	3.82	3.78	3.34
Cornet weight	1.375+	2.35+	2.425−
Gold lacking	2.445	1.23	5.765
Gold from solution	0.125	0.20	0.200
Gold from cupels	2.14	1.49	5.56
Balance	0.18−	0.46+	0.005−

From these figures it is evident that there is no necessity for running coin gold, and by fair inference fine gold, at such a heat as to favor the volatilizing of gold during cupellation. The high loss of weight of the cornets at the very high temperature could not be tolerated as a regular practice and such a temperature would not be used regularly.

Volatility of Silver

Silver is far more volatile than gold. Gmelin[36] states that it boils by the burning mirror when it rises in white fumes and that it volatilizes in

[36] *Op. cit.*, 138.

an open crucible at incipient white heat, but not if covered with charcoal dust. In a cathode-ray vacuum, Krafft and Bergfeld [37] observed volatilization at 680°. Johnston[38] gives its melting point as 960° and its boiling point as 2090°. He calculates that it has a vapor pressure of 10^{-3} mm. at 920° and 1 mm. at 1320°. In his atomic-weight work, Stas[39] distilled silver to purify it.

Richards[40] proposed to separate silver from blowpipe beads by volatilization. Over 95 per cent. of the silver was to be removed by heating before a sharp-pointed oxidizing flame to 1100°–1200° estimated and the balance removed at about 1500° estimated at which temperature the gold begins to volatilize. In a subsequent paper,[41] on measuring buttons, he said "It is difficult to drive off all the silver as the last 5 or 10 per cent. volatilize slowly and probably also take a little gold with them," furnishing an excellent illustration of the drag of a volatilizing metal upon a less volatile associate as well as the stabilizing effect of a less volatile metal upon a volatilizing one.

In a little-known and short-lived journal,[42] Seamon and Parker describe extensive tests on cupellation. As a preliminary, they made many tests on beads of silver 999 fine, of various weights up to 80 mg. for various times up to 4 hr., at various temperatures 900° to 1600°, by simply heating them in cupels. At the conclusion of the heating all the cupels showed a brownish spot below the beads. Several cupels were tested qualitatively for silver, which was always found. They proposed to make quantitative determinations of the silver absorbed, but I have not found such results published. The results are somewhat irregular. In one set of eight, on beads 5.09 to 22.50 mg. at 900° to 1000° for ½ hr., each one showed a loss of 0.02 to 0.07 mg., while another set of six, 20 to 80.06 mg. at the same temperature for 1 hr. showed no losses. They conclude that at 1000° "the loss appears to be mainly due to the oxidation of the silver and absorption of the oxide by the cupel," but at high temperatures volatilization may become important. Under their conditions 960° to 1020° barely gave feathers in cupellation.

I have done much work in checking up and extending this line of tests. Seamon and Parker appear to consider 999 silver as entirely satisfactory, but it is far from being pure and the impurity might influence the result. I used five grades of silver: proof of the highest purity, parting silver of

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[37] *Op. cit.* [38] *Op. cit.*

[39] *Mem.* Acad. Roy. de Belgigue (1865) **35**. See Crookes' "Select Methods," 282.

[40] *Jnl.* Frank. Inst. (1898) **141**, 447.

[41] *Jnl.* Amer. Chem. Soc. (1901) **23**, 209.

[42] *Bull.* Missouri Mining Club (1895) **1**, 16. It should be noted that in this paper per cent. losses are figured upon the weight of the resulting bead and not on the weight of silver taken.

high grade but not up to proof, ordinary silver reduced from the chloride by zinc, 50 gm. parting silver melted with 50 mg. lead, 50 gm. parting silver melted with 50 mg. copper. Under small beads it was only with the copper sample that the stain was plainly visible. With large beads four of the silvers stained the cupel and sometimes adhered closely to it; parting silver was not tested on large beads. Both large and small beads often showed a white coating. The figures showed irregularities and were larger than Seamon and Parker found, but I was forced to the conclusion that it was futile to expect to obtain exact or even comparative figures and discontinued the tests.

Exposure of molten silver to the air leads to a mixed result. There is oxidation of the silver and maybe volatilization. The oxidation products may be absorbed by the support in part only and part may remain in or on the metal. The loss shown by weighing the silver before and after such exposure cannot lead to definite results on any point.

Relations of Silver and Oxygen

Many and most contradictory statements have been made regarding the relations of silver and oxygen, both chemical and physical. The subject is greatly in need of clarification. It is apparent that they unite in various proportions.[43] While Ag_2O loses oxygen at very low temperatures and is said to be entirely decomposed[44] below 350°, pure silver prepared in the ordinary way gave off oxygen at 400° to 500° for 6 hr. at the rate of 57 cc. for a kilo of silver.[45] Silver and oxygen certainly combine at much higher temperatures and separate on lowering the heat.[46] Watts[47] says there is an oxide of silver volatile at high temperatures. Possibly this is based upon Plattner,[48] whose statements are questioned by Percy[49] and were further investigated by Christy.[50] Wartenberg[51] found silver appreciably more volatile in oxygen than in nitrogen and attributes this to the formation of silver oxide at high temperature, which may then possibly exist as a gas owing to its high heat of vaporization. Various writers have stated that sublimed silver often contains oxide of silver.

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[43] Watts *Dict.* **5**, 302; Roscoe and Schorlemmer, **2**, pt. 1, 367; Brown: *Trans.* Am. Electrochem. Soc. (1916) **30**, 327; Weber: Idem. (1917) **32**, 391.

[44] Percy: *Op. cit.*, 8 et. seq.; Thorpe's *Dict.* **4**, 700.

[45] Watts *Dict.* **8**, pt. 2, 1798.

[46] Percy: *Op. cit.;* Donan and Shaw: *Jnl.* Soc. Chem. Ind. (1910) **29**, 987. Watts *Dict.* **5**, 278 and others.

[47] *Dict.* **5**, 278.

[48] "Röstprozessen," 121. 1856.

[49] *Op. cit.*

[50] *Trans.* (1888) **17**, 6, 7.

[51] *Zeit. Electrochem.* (1913) **19**, 482; *Zeit. Anorg. Chem.* (1912) **79**, 76. See *Jnl.* Amer. Chem. Soc. (1914) **26**, 234.

Troost and Hautfeuille[52] say protoxide of silver exists in the very hot gases. Gmelin says "Silver at a white heat decomposes aqueous vapor . . . taking up oxygen," but on the next page says "silver does not oxidize in dry or moist air at any temperature below its boiling point." He also says silver "is less oxidized than platinum by fusion in the air."

T. K. Rose[53] says "even platinum was much more readily oxidized than silver," but in a previous paper[54] on refining by blowing air through molten bullion and fluxing the oxides produced he brought bullion 354 fine in gold and 621 fine in silver up to 885 gold and 103 silver. In comparing his process with cupellation, he says "later when the percentage of silver is high, it is freely oxidized in both processes, and the oxidation is at its maximum when the silver is practically pure." He says the "whole trend" of his work "is to show that it is silver that carries oxygen to base metals" and does not consider base metals oxygen carriers to silver. In this he appears to be dominated by theoretical considerations regarding normal oxides, Ag_2O and PbO for instance, and to overlook the possible interaction of other oxides.

The well known spitting of silver in solidifying has been generally assigned to the evolution of oxygen, but it has also been ascribed to the compression[55] of the solid crust on the molten interior. Having cooled large buttons, 7 to 10 gm., with extreme slowness and having obtained projections in the general form of a large irregular, inverted, hollow cone, in some instances only one cone on a button, I am satisfied that compression contributes to the spitting of solidifying silver. I have also produced spitting by the sudden cooling of a bead by contact with a mass of cold iron. In this connection it is certainly significant that silver melts and solidifies at a lower temperature in oxygen than in a reducing atmosphere.[56] Aside then from the natural cooling and solidifying of the surface first, the interior retains a lower melting point and remains liquid longer than the exterior, which has lost oxygen with the consequent raising of the melting point. The non-spitting of silver containing other metals may be due to changed differentials in the melting points.

Volatility of Lead

Johnston[57] gives the boiling point of lead as 1640° and the vapor pressure as 1 mm. at 960°. Kraft and Bergfeld[58] give 335° as their lowest

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[52] *Compt. Rend.* (1877) **84**, 948.
[53] *Trans.* Inst. Min. and Met. (1913–4) **23**, 173–4.
[54] *Idem.* (1904–5) **14**, 377, 420, 440–1.
[55] Mitchell: "Manual of Practical Assaying," 480. 1872.
[56] Ruer: "Metallography," tr. Mathewson, 296.
[57] *Op. cit.*
[58] *Op. cit.*

observation of volatilization of lead in a cathode ray vacuum. Schuller[59] and Kahlbaum, Roth and Siedler[60] distilled lead in vacuo and the latter obtained a crystalline product. Roberts[61] showed that with proper care there was no appreciable volatilization of lead in melting assay samples of base bullion. From the distillation of alloys, Moissan and Watanabe[62] announced that the order of distillation is lead, silver, copper, tin. The litharge cloud that is given off during cupellation is very deceptive. It makes an impressive showing in the muffle but the actual weight of oxide of lead is slight.

More than 50 years ago, Mitchell[63] announced that in the ore-assay cupellation "not more than 2 to 3 per cent. of lead is volatilized;" I have abundantly verified this statement. By weighing the cupels before and after use, I have found that it is quite possible to run an ordinary 20 gm. button with the volatilization of about 0.5 gm. of lead. This, however, involves some risk of freezing and requires much attention. At only a slightly higher temperature, with an increase of the volatilization to 0.75 gm., there is no risk of freezing and the operator may simultaneously look after other things. When the volatilization rises to 1 gm. there is but slight feathering unless special condensing arrangements are used. In one test, three cupels of the front row showed less than 2.75 per cent. volatilized and the fourth froze, while the second row of four showed from 5.5— to 6— per cent. volatilized and there were few feathers. With larger buttons, 50 to 60 gm., seven cupels showed less than 2 per cent. volatilized with a minimum of 1.4 per cent. In the cupellation of bullion,[64] where necessarily a higher temperature is used, the volatilized lead should not exceed 10 per cent.

Most contradictory statements have been made regarding the volatility of oxide of lead. The assayers' daily experiences disprove the statements of various textbooks as to its volatilizing only at a high temperature. The books appear often to be speaking of boiling[65] rather than simple volatilization. However, the boiling point, 870°, given by Mott[66] is palpably much too low. Doeltz and Grauman[67] say volatilization was slight at 800°, increased rapidly to 900°, when it became liquid, not so rapidly to 950° and was not tested above 1000°. By changing the ratio of surface to mass, they varied the loss from 8.8 to 0.04 per cent. at 900°.

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[59] *Wied. Ann.* (1883) **18**, 321.

[60] *Zeit. Anorg. Chem.* (1902) **29**, 278; *Bu H. Zeit.* (1902) 296.

[61] *Trans.* (1898) **28**, 425.

[62] *Compt. Rend.*, **144**, 16.

[63] *Op. cit.*, 484. Tests are given by Lodge: "Notes on Assaying," 56, and Liddell, *Eng. & Min. Jnl.* (1910) **89**, 1264.

[64] *Trans.* (1918) **59**, 214.

[65] Wagner: "Die Metalle," 111. 1866.

[66] Am. Electrochem. Soc. pamphlet, 1918.

[67] *Metallurgie* (1906) **3**, 406.

Feathering as an Indication of Temperature Conditions

Feathering is not always a sure indication of the temperature conditions of the bead. With high bead temperature and an abundant air supply the cupel may show good feathers, while the same bead temperature with limited air supply would not. Lack of feathers, particularly on inside cupels, may be due to lack of cooling conditions above the cupel, instead of high bead temperature. In two well-feathered cupels, Hillebrand and Allen[68] found 0.05 mg. loss of gold on 10.67 mg. cupeled, but only 0.03 mg. on 15.56 mg. The cupels immediately behind these showed 0.06 and 0.17 mg. losses, respectively. Lack of feathers may also be due to a leaky muffle.

Effect of Other Metals on Volatilizing of Gold and Silver

When true volatilization occurs in quantity, the volatilizing metal exerts a drag upon its less volatile associates, but the real data upon the subject indicate that in the vast majority of cases this drag is but slight. Bodemann and Kerl[69] say silver is often disposed to volatilization by arsenic, antimony, zinc and lead.

T. K. Rose[70] says that the presence of zinc, arsenic, antimony, and other volatile metals is believed to greatly increase the volatilization of gold, but gives no data. Hellot[71] says an alloy of one part gold and seven parts zinc volatilizes completely at a high heat, but Friedrich[72] investigated the subject and reported fifteen tests, from which he concluded that the loss was mainly due to mechanical action and it is only with rapid volatilization of zinc that the gold volatilization becomes appreciable. Up to 1500°, the loss was so slight as to warrant the conclusion that zinc has no influence in promoting the volatilization of gold below this temperature. I have shown[73] that in distilling the zinc out of Parkes crusts, very little silver goes over in proper work and that volatilizing lead carries but slight amounts of silver. I have also shown[74] that irregular assay results may be due to zinc carrying the precious metals to the surface of the cupel. It may well be that arsenic and antimony cause irregular assays in the same way rather than by volatilization. I have shown, too, that[75] the roasting of rich arsenide ores at a low heat produced arsenious oxide practically free from silver. In some recent tests we have obtained much more concordant results than those reported on arsenical bullion.[76] The assays were run in sets of six, two rows of three cupels with proofs in the

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[68] *Op. cit.*, 21.
[69] "Assaying," Tr. Goodyear, 103. 1878.
[70] *Jnl.* Chem. Soc. (1893) **63**, 714.
[71] Gmelin-Kraut: "Handbuch Anorg. Chem.," **3**, 1039.
[72] *Zeit. Anorg. Chem.* (1893) **16**, 269.
[73] *Eng. & Min. Jnl.* (1919) **108**, 87.
[74] *Trans.* (1918) **58**, 85.
[75] *Op. cit.*
[76] *Trans.* (1909) **40**, 795.

center; two sets were run on 5 gm. lead and one on 8 gm. on each bullion. The results were:

No. 1.		No. 2.	
Gold	Assays	Gold	Assays
665.5 fine	1	811.3 fine	1
665.6 fine	2	811.4 fine	2
665.7 fine	4	811.5 fine	3
665.8 fine	4	811.6 fine	1
665.9 fine	6	811.7 fine	3
666.1 fine	1	811.8 fine	5
		812.0 fine	3
	18		18

The arsenic in No. 1 was high but unknown, in No. 2 it was about 10 fine with, approximately, 90 each of silver and copper.

It is often claimed that tellurium promotes volatilization in cupellation, but T. K. Rose[77] carried on an extensive series of test under many conditions and in only one was gold found in the condensed tellurium. Holloway and Pearse[78] say "loss by direct volatilization is very slight under proper conditions of working" and on cupeling beads containing tellurium with proofs without tellurium in side by side cupels some tellurium beads lost less than the proofs.

In retorting gold amalgam, Rose[79] states that about 1 gr. of gold goes over per pound of mercury. Although outside the scope of this paper it may be mentioned that the recent volumes of *Transactions* of the American Electrochemical Society contain much interesting information regarding the action of metals, alone or mixed, at the very high temperature of the electric arc; and in 1907, Watts reviewed the work of Moissan.

Determination of Silver by Cupellation

The method I used in following up the course of the gold in a bullion assay is not applicable to silver. The determination of silver by cupellation[80] is quite unreliable and with large amounts the absorption of silver by the cupel[81] is most erratic. On the other hand the determination of the base metals left in small beads is unsatisfactory unless we have an exceedingly large number of identical beads. In another connection, I have shown[82] that the straight assay of a silver bullion showed 987 fine, which corrected for the cupel absorption became 998.5 fine, while

[77] Br. Asso. Rpt. (1897) 623–4.
[78] Inst. Min. and Met., 17, 171.
[79] "Gold," 141.
[80] *Jnl. Ind. & Eng. Chem.* (1914) 6, 650, 728.
[81] *Trans.* (1918) 59, 191.
[82] *Jnl.* Amer. Chem. Soc. (1894) 16, 514.

cupellation with proof showed 999.3 fine. Liddell[83] gives some very interesting tests on cupellation, but he determined the "fineness" of his beads, and this was subject to the errors of the original assay. Both these tests lack conclusiveness.

L. Campredon's book[84] says that all the silver lost is absorbed by the cupel, but the tests lack the determination of base metals in the beads. G. Campredon[85] made three tests in duplicate at a high temperature, one set using five times as much copper as silver, but he made no examination of his buttons. His results varied from nothing to 2.10 per cent. on 100 mg. silver. He made two assays of his cupels; one for beads on the surface, which varied from 0.40 to 1.50 per cent., and one for absorption. Various other indirect tests have been made, but all lack important data. Some tests show a gain even when the recoveries of silver were not complete.

It remains then that the only way to determine the volatilization of silver in a cupellation is to collect the litharge volatilized and assay it for silver. Manifestly this is also the only real way to ascertain the volatilization of gold under assaying conditions. I started out to do this without interfering with the normal conditions of cupellation, but found it impossible to do so in an ordinary muffle in constant use for regular work. Various arrangements of temporary baffle plates proved inefficient condensers and in many cases the condensed litharge entered into combination with the plate material. While it is possible by the use of special cooling arrangements to grow a large crop of feathers on the cupel, once the fume got out of the cupel it was practically impossible to stop it. Of course with a small muffle provided with special condensing flues, such as a Cottrell tube, and running a large number of identical assays a good approximation may be obtained, but I did not have these conditions. Again, with the low rate of volatilization of the lead in a proper cupellation of an ordinary 20 to 30 gm. button, the best feather-growing arrangements will yield only insignificant amounts of litharge. Feathers are most deceptive; they bulk large but weigh light.

After various tests I made a very deep cupel with straight sides. In the early tests the condensation of litharge was erratic, varying from 0.2 to 1 gm. and considerable experimenting was required to develop a satisfactory procedure. With 100 gm. lead and 1 gm. silver 0.605 gm. litharge condensed, yielding 0.055 mg. silver; with 5 gm. silver 0.735 gm. litharge gave 0.26 mg. silver; with 133 gm. lead and 6 gm. silver, 0.97 gm. litharge gave 0.26 gm. silver; with 140 gm. lead, 2.11 gm. copper, 8.33 gm. silver, 0.465 gm. litharge gave 0.27 mg. silver. By using large amounts of lead, placing the cupel close to the front of the muffle and

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[83] *Eng. & Min. Jnl.* (1910) **89**, 1264.
[84] *Op. cit.*, 307.
[85] *Rev. Univ. des Mines* [4] (1904) **8**, 210.

filling in around it so as to force all the draft over the cupel, and by protecting the cupel from radiation from the muffle top, I was able to condense a gram or more of litharge for assaying. This is none too much, even when cupeling very rich lead.

A most serious objection to this method is that in time the surface of the bullion sinks out of sight. As one cannot see the end of the cupellation careful watching and much judgment is required in turning off the gas. In ten tests, six buttons weighed more than the silver taken, the maximum being 3.4 gm. on 1 gm. taken and the minimum 0.13 on 5 gm. taken. Of the four losses, the maximum was 0.46 on 5.81 gm. and the minimum 0.04 on 5.045 gm.

In general, 140 gm. of lead were taken, the smallest amount of gold used alone was 140 mg., which would correspond to 20 oz. per ton in a 20-gm. button from an assay-ton fusion. The largest was 1.4 gm., or 200 oz. per ton. The following results were obtained. In the last test only 105 gm. of the lead were oxidized.

Gold Taken, Grams	Litharge Recovered, Grams	
1.40	1.45 containing 0.09	mg. gold
1.40	1.176 containing 0.02	mg. gold
0.70	0.876 containing 0.01 −	mg. gold
0.140	1.213 containing trace	
0.140	0.725 containing speck	

A sample of the celebrated Mercur bullion, about 884 fine in gold and less than 8 fine in silver, 1.6 gm., yielded 1.185 gm. litharge containing 0.03− mg. gold. Samples of miscellaneous bullion, most of them presenting unusual difficulties in ordinary assay work, yielded the following results:

Bullion weight, Grams	Fineness		Recovered		
	Gold	Silver	Litharge Grams	Gold, Mg.	Silver, Mg.
3.5	808	34	0.92	None	Slight trace
2.5	585	95	1.45	Speck	0.02
2.5	585	316.5	1.312	Very slight trace	0.015
4.0	361	228.5	1.32	0.01	0.08
4.2	343.5	443	1.13	0.005	0.16
6.75	211	225	0.95	0.005	1.26

In the last test, a scum appeared early and crystals were slow in forming; probably some of the scum adhered to the feathers recovered.

With 1 per cent., 1.4 gm., gold, and 3 per cent., 4.2 gm., silver, 1.27 gm. feathers showed a very slight trace of gold and 0.21 mg. silver. In one test the lead carried about 1 per cent. arsenic, but the cupel cracked.

With 0.5 per cent. arsenic and 1.4 gm. gold, 1 gm. litharge was collected and the gold obtained was estimated at 0.002 mg.

Three grades of base bullion were tested—good, bad, and very bad for assaying. Using 159.5 gm. of the first gave a button weighing 1.24 gm., 0.762 gm. litharge was collected, which gave a bead of 0.08 mg. The second would not cupel direct, but 20.03 gm. were run with 152.45 gm. proof lead and gave a button weighing 3.475 gm., 0.975 gm. litharge was collected giving a bead of 0.08 mg. In a second test, the figures were bullion 20.62 gm., lead 142.45 gm., button 3.422 gm., litharge 1.322 gm., bead 0.28 mg. Probably the high litharge and bead were due to the early formation of an unabsorbed scum on the cupel, upon which later feathers formed, particles of which adhered to the litharge recovered. The third sample yielded the highest recovery of litharge of any test made, 1.50 gm., due perhaps to the same causes. The figures were, bullion 20.79 gm., lead 139.06 gm., button 3.25 gm., litharge 1.50 gm., bead 0.30 mg. Extreme tests were made on three grades of silver—proof, 900 silver 100 copper, 750 silver 250 copper. Starting with 2 and 3 per cent. actual silver on the 140-gm. lead buttons, the results were:

	2 Per Cent. Silver Litharge		3 Per Cent. Silver Litharge	
	Weight, Grams	Silver, Milligrams	Weight, Grams	Silver, Milligrams
Proof	1.04	0.24	1.28	0.26
900	1.16	0.20	0.97	0.26
750	1.24	0.21	0.71	0.21

DISCUSSION

J. W. Richards,* Bethlehem, Pa.—The volatilization of the metals in assaying is a special case of differential volatilization and is dependent on the different vapor tensions of the different metals. Combined with this volatilization, however, there is usually the formation of mist, which must also be taken into account and, I think, explains some of the inconsistencies pointed out in the paper.

For instance, Doctor Dewey has shown that more silver goes off with zinc in the early stages of a distillation, in which zinc-silver alloy is distilled. According to the vapor tensions of the zinc and the silver, more should be going over in the later stages. That discrepancy is to be explained by the fact that in the early stages of the distillation there is probably a more rapid formation of zinc vapor, and that it carries away, as it escapes in the form of bubbles, a larger amount of the alloy in the form of mist. Now, the alloy that is being distilled carries a larger percentage of silver than the distillate, or the vapor that is going off; for

* Professor of Metallurgy, Lehigh University.

instance, the vapor going off may contain 2 per cent. of silver while the alloy itself may contain 20 per cent. Therefore, if some of the alloy is carried over by the rapid boiling off of the zinc, that alloy increases the richness, and apparently will increase the amount of silver that goes off. The amount of the volatile metal that goes off as true vapor can be determined exactly from the vapor tensions of the metals. But the amount that goes off as mist or fog, representing alloy carried off mechanically, may contain far different proportions of the precious metal than the vapor.

As far as I know, it is impossible to calculate just how much of a material will be carried off as fog or mist. The amount depends on the rapidity with which the material is boiled; it is like the water that goes over with steam. Perhaps if we analyzed all the conditions and got all the variables, we might commence to find the conditions that regulate the amount of mist or fog formed, but as yet our metallurgical data and physical analyses have not progressed that far.

On page 604, Doctor Dewey makes a statement that needs a little explanation: "There is absolutely no connection between melting point, vapor pressure, and boiling point." I admit that there is no connection between the melting point and the normal boiling points of the metals; some with a low melting point have a high boiling point and others with a high melting point have a low boiling point; but by boiling point, we mean boiling temperature of 760 mm. pressure, the normal boiling point. The statement that there is no connection between the vapor pressure and the boiling point needs a little amplification. That there is no connection between the melting point of the metal and the normal boiling point, I will admit, but the introduction of the term "vapor pressure" may be misleading.

The next line contains the statement that various metals show vapor pressure below their melting point. I wish to amplify that by stating that all metals show vapor pressure below their melting points. In fact, the question is not whether the metal shows vapor pressure, but simply whether it has been determined. I would even say that at ordinary temperature all metals have vapor pressures. The process of sherardizing by means of zinc dust depends on the vapor pressure of zinc below its melting point.

F. P. DEWEY.—I take complete exception to Professor Richards' closing statement; I do not admit that there is vapor pressure of all metals at all temperatures.

Coal-pulverizing Plant at Nevada Consolidated Copper Smelter

By R. E. H. Pomeroy,* E. M., McGill, Nev.

(New York Meeting, February, 1920)

Early in 1917, it became evident, owing to existing and pending market conditions, that a substitute for crude petroleum must be found for firing the smelter furnaces. After a review of the plants then existing, it was deemed advisable to depart from their practice and to adopt the following described system of distributing pulverized coal to the furnaces.

The principal advantages of the proposed system, which influenced this decision, were: (1) Equal safety; no pulverized coal is stored at the furnaces; (2) greater ease of operation, furnace fires being controlled by regulating valves in burner branches, as in gas firing; (3) better organization; all machinery, including pulverized coal feed, is under one roof, and the organization is separate from the furnace department; (4) greater cleanliness; all machinery is under vacuum; (5) greater flexibility of application; the coal and air mixture can be piped where needed.

The design of the plant is the result of the combined efforts of the local engineering staff and of the machinery manufacturers. Many new features were embodied in this design to insure greater safety, cleanliness, and efficiency of handling. After 14 months of continuous operation, the plant has proved entirely satisfactory.

The building is of structural steel, covered with corrugated steel, with many windows and is painted light gray inside and out. The building floor is of concrete with ample drains to the sewer, and the building is equipped with fire and service water piping. Fig. 1 shows the east side of the building and the incline conveyor from the raw-coal bins.

The plant is operated entirely by electric power. All alternating current is 550 volts, 3-phase, 60 cycles. The pulverized-coal feeding motors and control mechanism are operated by 220-volt direct current supplied by motor-generator sets in the building. Automatic push-

* Smelter Superintendent, Nevada Consolidated Copper Co.

button controlled switches are in use wherever possible. All power headers are located in the roof trusses, with branches in the conduit leading down to and under the concrete floor to the motors. All motors are

FIG. 1.—EAST SIDE MAIN COAL PLANT BUILDING SHOWING INCLINE CONVEYOR WAY FROM RAW COAL BINS.

direct-connected or drive through link-belt silent chains, or James speed-reducing transmissions running in oil.

The accompanying flow sheet, Fig. 2, gives a general outline of the installation.

Raw coal in storage bins *A* is received in standard cars over railroad track scales, and delivered to the bins on a steel trestle spanning the bins, the supports of which are independent of the bin structure. This trestle is equipped with walkways and grizzlies *1* and either slack or mine-run coal can be received for pulverizing.

Storage bins *2*, eight in number, are of reinforced concrete with concrete partitions which subdivide them into fireproof compartments. Each bin is provided with two thermocouples which indicate, at a central station, the temperature of the coal. There are six pipes placed vertically in each bin, through which temperatures are taken with a thermometer. Even though the coal is over 22 ft. (6.7 m.) deep, when the bins are full, we have been able to prevent spontaneous fire by drawing off the coal wherever heating commences. The bottoms of the bins slope toward the center at an angle of 35°, which has proved a little too flat for self cleaning. At the bottom of the slope, at the center, are 64 steel chutes with cast-iron basket gates *3* which

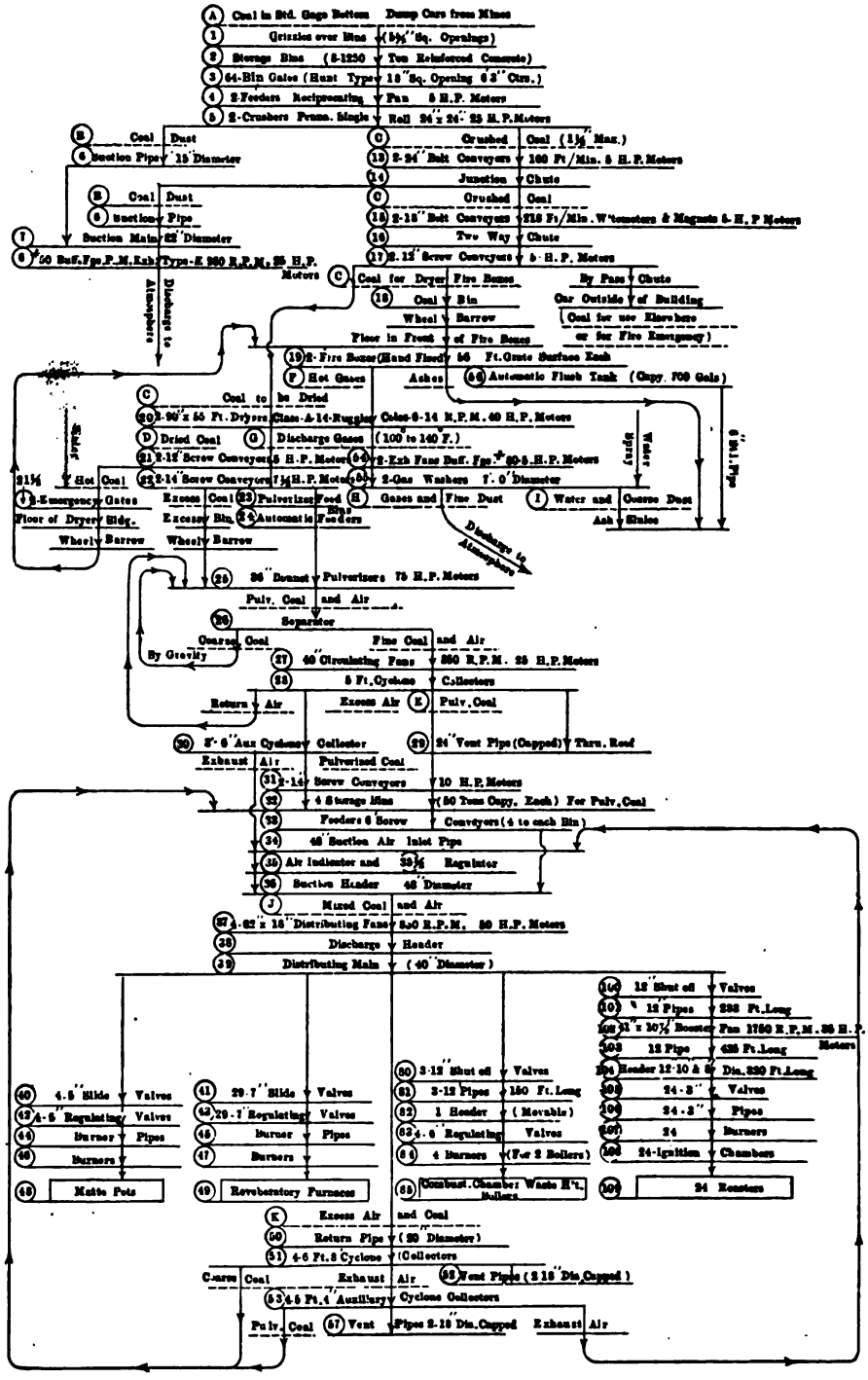

FIG. 2.—FLOW SHEET.

deliver the raw coal to the feeders *4* located one on each of two portable cars in a tunnel under the bins. These feeders are operated by variable-speed motors, the speeds of which are regulated according to the number of pulverizers operating in the main plant. Each feeder discharges into the jaw of a single-roll coal crusher *5*, also mounted on the portable cars, so that when mine-run coal is fed it emerges from this machine as slack.

At this point *B*, it was found that a dangerous accumulation of coal dust was formed. Suitable suction piping *6* was attached to the crusher cars and connected *7* to the intake side of a fan *8* located outside of the

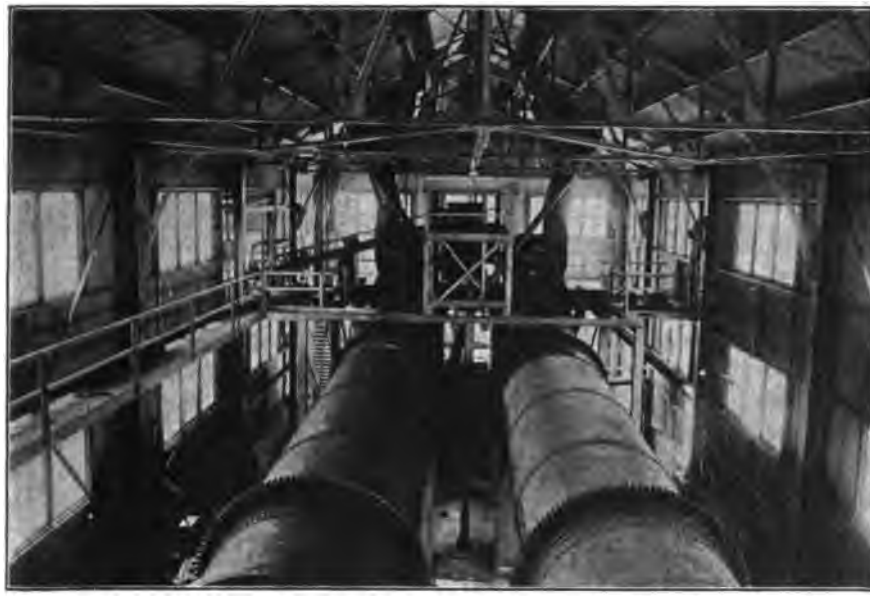

FIG. 3.—FEED END OF RUGGLES-COLES DRIERS, SHOWING INCLINE CONVEYOR FROM RAW COAL BINS.

structure. This eliminated the dust nuisance which, while very small in quantity, was a considerable hazard if allowed to accumulate at its inaccessible source. This fan discharges to the atmosphere.

The crushed coal *C* falls on to a conveyor belt *13*, which transports it to a junction chute *14* near the center of the bin structure, where it falls on to one or both of two incline conveyor belts *15*, which convey the coal, over Merrick weightometers, to the main building. Suction piping connected to the fan *8* prevents dusting as coal falls on to the incline conveyors. The discharge from the incline conveyors falls into a two-way chute *16*, with positive splitter, which deflects the stream to either or both of two screw conveyors *17* feeding the Ruggles-Coles type A-14 dryers *20*. Fig. 3 shows the feed end of the dryers, with the incline conveyor from the raw-coal bins.

The coal required for firing the dryers is taken at this point into a small coal bin or tank *18* from which it is wheeled to the fireboxes, and fired by hand. The original arrangement provided a chute which delivered the coal from the screw conveyor directly to the firebox, but this did not prove entirely satisfactory, since it gave no means of determining the amount of coal burned in the drying operation, and was abandoned. Pulverized coal could be used for firing the dryer, and this may be done later, if a saving can be shown. The dryer consumes approximately 0.75 per cent. of the coal dried.

A bypass chute is attached to one end of one of these screw conveyors *17* through which coal can be moved out through the side of the building into a standard railway car, to be used elsewhere, or for the removal of coal from the concrete bins in case of fire in the raw coal.

The gases from the dryer *G* pass through an induced-draft fan *54* and are discharged through a gas washer *55* to the atmosphere *H*, while the wash water *I* is passed to the sewer. The ashes *56* falling through the dryer grate are flushed away intermittently, to the sewer, by a stream of water from an automatic flush tank, the water used being waste water from the power plant.

Dried coal *D*, on leaving the dryers, discharges through dust-tight housings into screw conveyors *21*. At this point provision has been made to discharge coal on to the floor through an emergency gate, and to wet the coal in the conveyor *21* should the dryer become overheated and the coal catch fire. From the dryer discharge conveyors *21* the coal falls into two longitudinal screw conveyors *22*, which move it to the pulverizer feed bins *23*. At the point where the coal falls between the conveyors *21* and *22*, is inserted the bulb of a Bristol recording thermometer, the record of which is used as a guide in operating the dryer. Moisture samples of the coal entering and leaving the dryer are taken every half-hour, and as the discharged-coal sample is taken by hand, this also serves to prevent overheating of the dryer in case of failure of the thermometer. As a further precaution against overheating, the power leads to the induced-draft fan are taken off beyond the switch to the dryer motor, so that the fan motor can be run only when the dryer is in operation, and is shut down with the dryer, although the dryer may revolve without the fan being in operation.

The coal from the conveyors *22* falls into four hoppered bins of small capacity, from which it is fed to the pulverizers *25* through feeders *24*. The feed of slack coal to the pulverizer is regulated by the electrical load on the machine, as indicated by an ammeter. The pulverizers are 36-in. Bonnot mills, seven in number, with places provided for eight. Fig. 4 shows the interior of the mill with the driver exposed. As is common practice with other types of pulverizers, the coal is drawn out of the mill by a current of air, is passed through a separator *26*, circulating fan

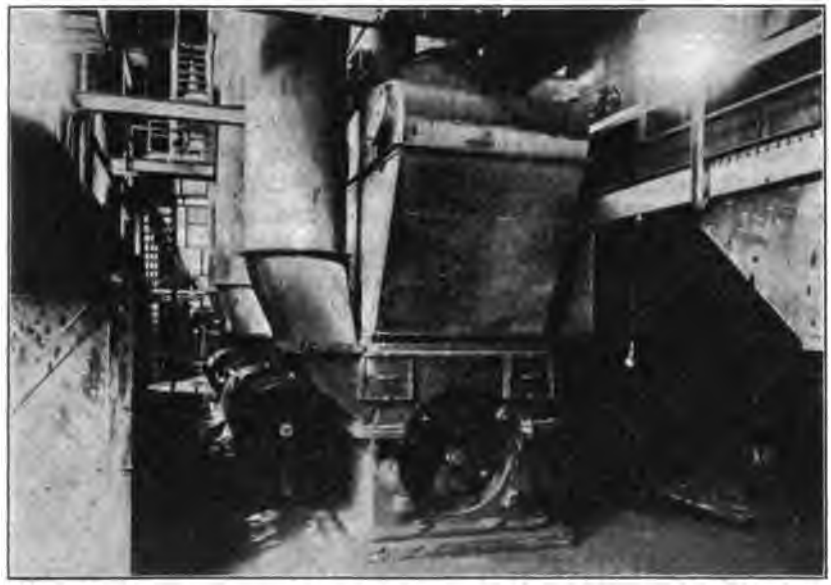

FIG. 4.—BONNET PULVERIZER WITH END PLATE REMOVED, EXPOSING DRIVER.

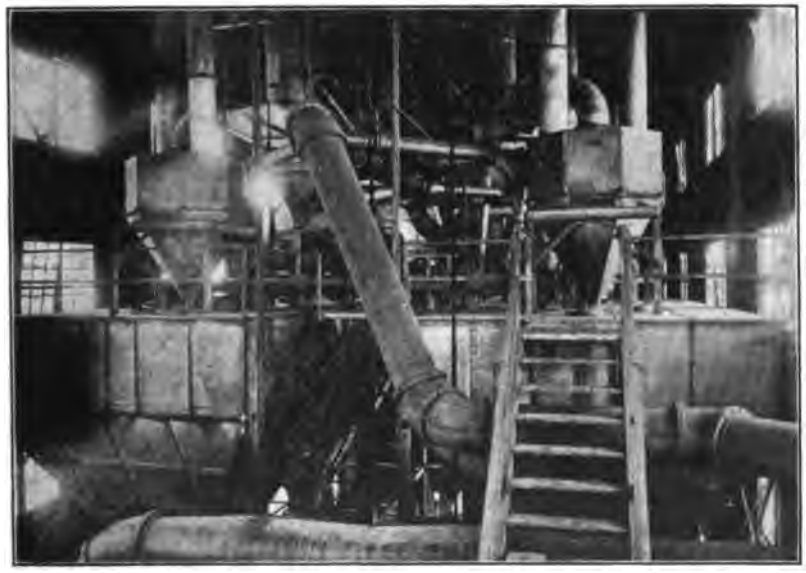

FIG. 5.—TOP OF 50-TON PULVERIZED-COAL BINS SHOWING RETURN LINE WITH BRANCHES TO RETURN LINE COLLECTORS.

27, and into main and auxiliary dust collectors *28* and *30*. The air returns to the mill and the coal *E* falls from the collectors to screw conveyors *31*.

The only difference between this system and current practice is that the latter vents the excess air from the auxiliary collectors *30* to the atmosphere; while the excess air here is piped from the auxiliary collectors to the main suction header *36*, described later. The vents *29* are capped above the roof and serve only as safety valves in case of explosion.

The screw conveyors *31*, below the collectors *28* and *30*, carry the coal *E* to the 50-ton pulverized-coal storage bins *32*, four in number. These are provided with emergency explosion doors and compressed-air kicking devices to prevent hanging up, and are calibrated to measure the contents from the floor, at will. Fig. 5 shows the top of the 50-ton bins.

FIG. 6.—PULVERIZED-COAL FEEDING MECHANISM TO SUCTION HEADERS. SUCTION SIDE DISTRIBUTING FANS IN BACKGROUND.

From a cast-iron hopper at the bottom of these bins, the coal is drawn off by the pulverized-coal feed screws *33*, four per bin, and dropped into the air-current in the main suction header *36* leading to the distributing fans *37* as shown in Fig. 6. These feed screws are driven through roller chains by direct-current, variable-speed motors, the speed of which is regulated by a sheet-metal cone floating in the air current in the main suction header *36*, and known as the indicator *35*. This device is connected, by light cable over sheaves, to the regulator mechanism *35½*, which, through a rheostat, governs the speed of the feeder motors in proportion to the amount of air flowing in the suction header (see Fig. 8). The pro-

portion of air to coal may be varied within limits, but it has been found best to maintain a ratio of 50 cu. ft. (1.4 cu. m.) of air to 1 lb. of pulverized coal (3 cu. m. air per kg. of coal). An instrument attached to the indicator continuously records the rate at which the air is flowing, and revolution counters record the operation of the feed screws.

The suction header *36* is connected to the auxiliary pulverizer collectors *30*, before mentioned, and to the return-line auxiliary collectors *53*, described later, and draws the necessary make-up air from the top interior of the building, through a gooseneck extending up through the roof and down again to the indicator *35*. Thus all dust-producing points

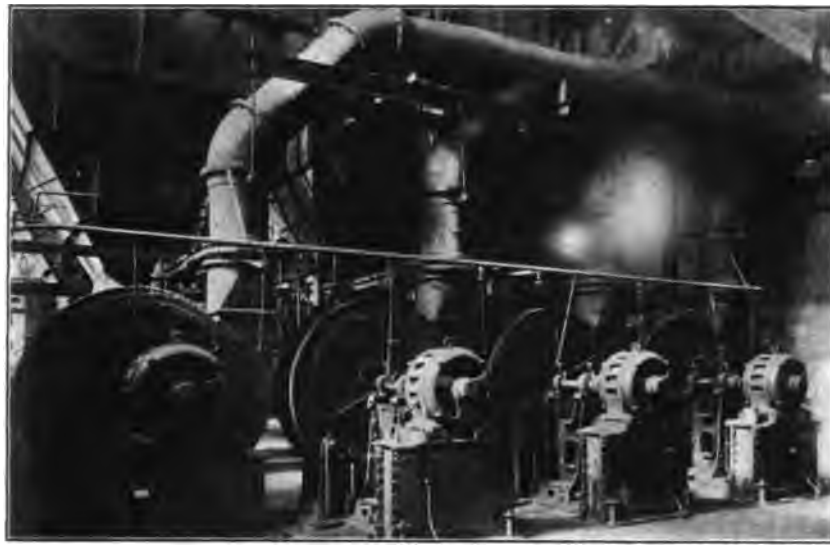

FIG. 7.—DISTRIBUTING FANS, MOTORS, DISCHARGE HEADER AND DISTRIBUTING HEADER.

are exhausted by vacuum, and the building is automatically ventilated. This header is amply provided with explosion doors, as the coal mixture is lean and explosive. The 50 to 1 mixture is too rich to explode, and hence this precaution is not needed on the distributing header *39*.

The distributing fans *37*, receiving the proportioned air and coal through the suction header *36*, discharge the mixture *J* through the discharge header *38* to the distributing header *39*. Fig. 7 shows the arrangement of fans, motors, discharge, and distributing headers.

The distributing header leaves the coal plant and passes along the firing end of the reverberatory furnaces at a convenient distance from and above them. Opposite each furnace, a 7-in. (18-cm.) drop-pipe leaves the bottom of the main through a slide gate *41*, regulating valve *43*, burner pipe *45*, and burner *47*, to the firing-wall opening in the furnace *49*. The main distributing header *39* is reduced in diameter after each fur-

nace take-off, in order to maintain the velocity requisite to prevent settlement of the suspended coal dust. After serving the reverberatory furnaces, the header makes a 180° turn upward and backward, returning to the coal plant the remaining mixture *K* through the return header *50*.

The return header enters the coal plant and divides into branches which lead to the return-line dust collectors *51* and to the return-line auxiliary dust collectors *53* (Fig. 5). These collectors are situated above the 50-ton pulverized-coal bins *32*, and the coal removed from the mixture

FIG. 8.—AIR INDICATOR AND COAL FEED REGULATING DEVICE.

K is thus returned, to be fed again to the suction side of the distributing fans *37*. The quantity returning varies from 10 to 100 per cent. of the total coal *E* fed to the suction header *36* depending on the amount of the mixture *J* being taken off by the furnaces. Thus, even though no coal is being taken off for burning, the coal in the 50-ton bins is being constantly turned over, preventing spontaneous heating, so long as the distributing fans are in operation. The return air, relieved of most of its burden of coal dust, passes from the auxiliary return-line dust collector *53* through a

header pipe to the main suction header *36*, joining the latter above and before passing through the indicator *35*. See upper left-hand corner of Fig. 8.

This completes the cycle through which the main bulk of the coal passes. Further application of coal-dust firing to other departments is made in the following manner.

Taking off from the main distributing header *39*, on the bottom of the pipe, are four 5-in. pipes, located at intervals, where required, between the coal plant and the point where the main distributing header *39* turns back as the return header *50*. Each take-off is provided with a slide gate *40*, a control valve *42*, burner pipes *44*, and burners *46*, and the fuel is used intermittently for firing portable matte-transfer cars *48*.

Taking off at the end of the main distributing header *39* is a 12-in. pipe, leading through a 12-in. gate valve *100* and thence 283 ft. to a booster fan *102* which is 41-in. (104 cm.) in diameter and runs at 1750 r.p.m. The discharge from this fan, at increased velocity and pressure, passes through 435 ft. of 12-in. pipe *103* to the roaster plant. Here it passes along one side of the building for 320 ft. as a header *104* and is tapped for each furnace through 3-in. (7.6-cm.) take-off pipes, valves *105*, etc. The main is tapered as it advances, to maintain a carrying velocity, and there is no return line.

This extension is quite recent, but has not given much trouble if enough burners are kept in operation to prevent the line from choking up with coal dust. A return-line system would work more smoothly, but would require a larger main line, for the same capacity, as well as a return line with a booster fan.

During the period of high-pressure operations, while the war was on, it became necessary to utilize every boiler in the plant. Take-off pipes (12-in.) were installed at suitable places along the main header, and branch pipes were run through shut-off valves *80* to the waste-heat boilers located in the flues of the reverberatory furnaces, a distance of about 150 ft. Pulverized coal was burned, for months, under all boilers in the flues of such furnaces as were idle or down for repair. No efficiency tests were made, and pipe sizes and velocities were not correctly proportioned, but the flexibility of the system was clearly demonstrated.

To the end of July, 1919, the plant had pulverized 173,230 tons of raw coal. The power consumption for the entire operation has been about 30 kw.-hr. per ton of raw coal pulverized. It must be borne in mind that any comparison of this figure with the power required for other systems must take into consideration the power devoted to the production of blast, usually furnished from an outside source, by which the dust is blown into the furnace.

The wear has not been excessive, considering the nature of the service, and has been confined almost entirely to the fan wheels and housings.

Ample provision has been made for repairs, and no operating time has been lost while making repairs due to wear.

The capacity of the pulverizers is from 4½ to 5 tons per hour, and the plant was operated for six weeks at an average daily rate of 550 tons of raw coal. Owing to the large storage capacity for pulverized coal in the 50-ton bins, it is necessary to man the pulverizing plant only one or two shifts out of three, when not burning over 300 tons daily.

DISCUSSION

B. F. TILLSON, Franklin, N. J.—I would like a little more engineering information than is given in this paper. The size of the mains is given but not the length. It would be of interest to be able to figure the friction losses in the pneumatic transport of pulverized coal, in order that those figures may be used in the layout of other plants. I trust that the author has such data, or will be able to add such information in the discussion of this paper, giving any tests he may have made in regard to pressure drops that have occurred in some unit length of pipe, and the minimum air velocities that have been necessary in order to convey the coal in suspension.

On page 625, he says that a ratio of 50 cu. ft. of air per pound of pulverized coal has proved the best. Recently, I was informed that 90 cu. ft. of air per pound of coal was the proper ratio; it makes a good deal of difference in the design of the pipes in such a system which of these figures are being used.

Another question that has arisen is why the burning of pulverized coal has been evidently free from the danger of flare-backs in the burner nozzle. Some figures that I have seen, from the experiments of the United States Bureau of Mines in regard to coal-dust explosions, indicate that the minimum velocity of propagation of an explosion of coal dust is about 200 ft. per sec., and that in four seconds it increases to over 2000 ft. per sec. The pressures that I have seen in some plants have been a 2-in. water head at the fan, which is injecting the coal through the burner into the fire; and if all of that static pressure were changed into velocity pressure and velocity, it would give a maximum of 5664 ft. per min.; and if the velocity of propagation of explosions reaches from 200 to 2000 ft. per sec., and the coal dust is mixed in the pipe with sufficient air to support combustion, why does not the explosion come back in the main line?

R. E. H. POMEROY (author's reply to discussion).—The diameter of the main distributing pipe leaving the coal-pulverizing plant is 40 in.; returning to the coal pulverizing plant it is 20 in. The reductions are made at the burner take-offs to each furnace. The total length of main and return lines is, approximately, 850 feet.

It is difficult to measure the pressure of a current of air in which coal dust is suspended. In this particular installation, the closest approximation of the pressure at the fan delivery was between 6½ and 7 oz. At the extreme end of the line (where the main line bends to return) the pressure was approximately 2½ oz. The pressure at the return-line dust collectors was practically atmospheric, and at the discharge of the dust collectors a slight vacuum obtained.

The line was designed to be operated at a mixture of 50 cu. ft. of air per pound of coal and was so operated for many months. Under certain conditions, the line was operated at a mixture of 30 cu. ft. of air per pound of coal for considerable periods. The regulating machinery, however, was designed for the first mentioned figure, which is ample to distribute the coal and is well within the safety limits.

A velocity of 3000 ft. per min. is necessary to insure transportation of the suspended solid particles of coal dust (this figure to be the absolute minimum); 4000 to 5000 ft. per min. is preferable for working conditions. The velocity through the burner nozzles into the furnace has never been measured, but I would estimate it to be between 4000 and 6000 ft. per min., which is more rapid than the propagation of flame.

Another explanation why the flame does not flare back into the burner pipe is that the mixture of 50 cu. ft. of air per pound of coal is too rich in coal dust to deflagrate.

In my two years experience with this system, in which time considerably over 200,000 tons of coal were pulverized and distributed, I have not known of a case where the mixture of pulverized coal and air was deflagrated back to the distributing main. It is not even possible, in normal operation, to bring the burning action or deflagration of the coal dust and air mixture within the furnace back to the tip of the burner.

Laboratory Testing of Sands, Cores, and Core Binders

F. L. WOLF* AND A. A. GRUBB,† MANSFIELD, OHIO

(Columbus Meeting, October, 1920)

THERE is a tendency on the part of practical foundrymen to accept with reluctance the results of tests on sands, binders, and such materials made in the chemical laboratory alone. They feel that such tests frequently emphasize and measure properties that are of minor importance and fail to take account of characteristics that are important in determining the value of the material in actual practice.

Experience seems to indicate that the most thorough and conclusive test for any new foundry material is an actual run in the foundry alongside of a standard material of known value. Such a test, however, involves certain difficulties and necessitates certain precautions. It is not always easy to obtain a fair trial for a new material. We all have certain prejudices, which unconsciously affect our judgment to a marked degree. A practical test frequently involves so many workmeh, each of whom reacts in a different manner to the test, that the personal equation becomes very complex and the true results of the test are obscured. There are times, too, when a thorough experimental trial of a material would interfere too much with the rush of work in a department or would hazard the quality of the product to such an extent as to make it inadvisable. Under such conditions a laboratory test is advisable before the material is sent into the foundry. These tests should be made as practical as possible and so closely related to foundry practice as to give a true index to the value of a product for the purpose desired.

Core sands and molding sands are as numerous "as the sands of the sea" and vary as much in quality. Old sources of supply are continually failing and new ones must be opened, so that we must continually search for new and better grades of sand. During the past year, the Ohio Brass Co. has developed tests for sands, cores, and binders which bear a close relation to the particular use to which these materials are put in the foundry and which are fairly indicative of their value. While the tests thus far have been confined to cores and core sands, it is expected that tests for molding sand will be developed in the future.

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For the purposes of this company, the chemical analysis of a sand appears to be of no great value. A drop of muriatic acid on a small sample and examination under a low-power microscope or pocket magnifying glass give sufficient information regarding the composition of a sand. Other characteristics of sands and cores have a greater effect on the quality of the castings and the percentage losses.

An Ideal Core

An ideal core must be strong enough to stand a fair amount of rough handling, without excessive breakage, not only when baked but before it is baked, in order to obtain speed in making and handling. This strength, however, must fail at the proper time. A temperature of from 1000° to 1200° F. should burn out the binder to such an extent that the core becomes very fragile and can be easily shaken out of the casting.

An ideal core should be open or permeable. Molten metal readily absorbs the gases given off as the metal solidifies. As the core is heated to the temperature of the casting, the binder too is burned out and partly converted into gas. This gas is frequently from ten to twenty times the volume of the core, which must be sufficiently open to allow all such gases to escape without causing blows. The ideal core will give off a minimum quantity of gas when burned. A smooth close-grained core is also desirable in the brass foundry, as there is a tendency on the part of some brasses to bite into the core.

The binder must not harm the hands of the core makers; it should possess no markedly disagreeable odors, and should not cause the green sand to stick to the core boxes, producing rough cores.

The ideal core for brass casting may be briefly described as follows: Fairly strong while green; very strong when baked; easily destructible when burned; smooth surfaced; very permeable; of low gas content; and should work easily and agreeably in the hands of the coremakers.

All of these qualities, however, cannot be obtained to a maximum degree in a given sample. Great strength and a smooth surface can be obtained only at the sacrifice of a certain amount of permeability, but some work that demands permeability does not require a smooth surface, so that sometimes one quality may be sacrificed for another.

Composition Test

A new sample of sand is first examined under a low-power microscope —preferably one of about ten diameters though a linen tester or pocket magnifying glass will serve as well. First the shape of the grains, whether angular or round, is noted. The former is called a sharp sand and the

latter a smooth one. Then the amount of silica or quartz, a constituent which is always desirable, is estimated. These particles usually appear as colorless or semitransparent bodies; sometimes, however, they are tinted with impurities. An abundance of red particles usually indicates feldspar, which is undesirable on account of its low melting point. Tiny semitransparent plates are mica chips, which burst apart when heated, producing a rough surface. Limestone usually appears as milky white particles; its presence can be detected by putting a pinch of the sand in muriatic acid, when tiny bubbles of gas will appear. Clay and organic matter are easily recognizable and their quantity can be roughly estimated under a microscope.

Fineness Test

The fineness test has two points in view—the average or degree of fineness and the grading of the sand. The degree of fineness, in a way, determines the smoothness of surface and the porosity of the core. It is well known, however, that two sands of equal fineness may have markedly different permeability. It is well, therefore, to know just how the sand is graded, whether it is nearly all of one or two meshes or if the grains are of nearly all sizes. Our method of making the determination is the standard one except that we start with the 200-mesh screen instead of the 100-mesh; it is the finer material, 150-mesh and 200-mesh, that gives the sand bond and decreases its permeability. A 100-gm. sample is shaken successively on the 200-, 150-, 100-, 80-, 60-, 40- and 20-mesh screens and the weight passing through each screen is recorded in per cent. of total. Each weight is then multiplied by the mesh of the screen through which it passed, that remaining on the 20-mesh screen being multiplied by one; the products are added and divided by 100. The result is taken as a measure of the fineness of the sand.

Permeability Test

While porosity and permeability are somewhat related they are by no means the same thing. By porosity, is usually meant the openness of a sand or the percentage of void space that a given volume contains. Permeability is a measure of the freedom with which a gas passes through the sand and is the property in which we are primarily interested. Assuming the sands to be composed of spherical grains of uniform size, it is well known that gas passes more easily through a coarse sand than through a fine one, yet it is a mathematical fact that the void space is the same in all cases.

Calculations show that a volume filled with spheres of uniform size and packed as closely as possible contains approximately 36 per cent. void space regardless of the size of the spheres. This void space, how-

ever, is cut down by mixing spheres of different sizes, the smaller ones filling in between the larger. Likewise with core sand, maximum openness can be obtained when the grains are of uniform size, or as nearly so as possible. To measure the permeability of a core or molding sand the following apparatus and method have been employed:

A water-column aspirator *A*, of 400 c.c. capacity is connected with a 6-in. U tube *B*, Fig. 1, by a flexible hose connection *C*; *F* and *D* are glass stop-cocks. The elbow *E* prevents bubbles of air from entering the water

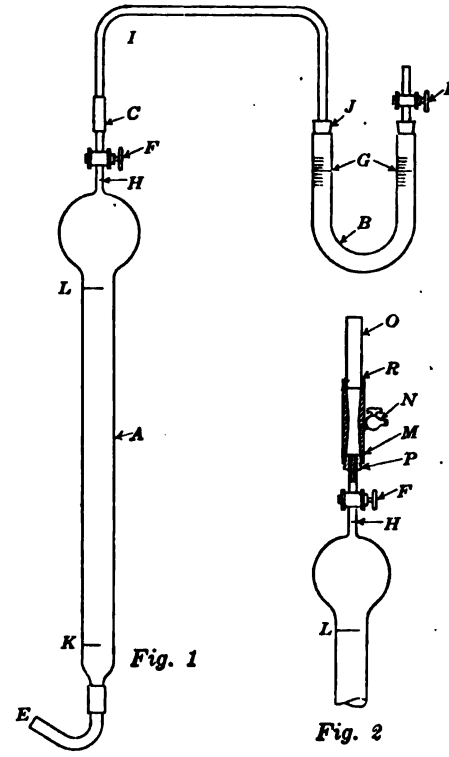

Fig. 1

Fig. 2

column. The sand under examination is placed in the U tube *B*, which is then shaken or tapped until the sand ceases to settle and stands even with the marks *G*. Before connecting at *J*, the aspirator column is filled with water, by means of a rubber tube connected to the faucet, and held with the fingers against the opening at *E*, the stop-cock *F* being open. When the water reaches *I* or thereabouts, the stop-cock *F* is closed and the connection made at *J*. The other stop-cock *D* (open) is now set in the other side of the U tube and then closed. The first stop-cock *F* is slowly opened allowing the air in the U tube and connections to expand and the surface of the water column to fall until it comes to an equilibrium. It is then adjusted to the mark *H* by carefully allowing

air to pass through the stop-cock *D*. When all is ready, this stop-cock *D* is opened wide and a stop watch started. The time, in seconds, required for the water level to fall to *K* is taken as the measure of the permeability of the sand. This figure is really inversely proportional to the permeability inasmuch as a highly permeable sand requires much less time than does one of lower permeability. For very close sands time may be saved by stopping the watch at the half-way mark *L* and then doubling the time.

No attempt is made to figure the results in absolute units; the method gives only comparative values for various sands. Results ranging from 30 sec., for very open core sands, up to 14,000 sec. for a very close mixture containing a considerable amount of dust, have been obtained. Results on the same sample can be duplicated within a few per cent.

The permeability test has given information that is not only interesting but valuable. Originally the fineness tests were made on screens ranging from 20 to 100 mesh; but two samples of sand were received that gave similar fineness tests yet differed widely in permeability:

Sample	100	80	60	40	20	1	Fineness	Permeability
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.		
1.....	35.4	14.6	14.7	22.1	12.1	1.1	67.2	6660
2.....	35.5	14.5	15.1	22.2	11.5	1.2	67.4	4000

This was difficult to explain until the 100-mesh material was examined on the 150- and 200-mesh screens. Of sample No. 1, 8.1 per cent. went through the 200-mesh, 12.3 per cent. through the 150-mesh and 15 per cent. through the 100-mesh; while of sample No. 2, practically all remained on the 150-mesh screen. This led to the use of the 150-mesh and 200-mesh screens whenever accurate information was desired. It must be remembered that the use of these finer screens materially changes the degree of fineness figures so that they are not comparable with the figures made using the screens from 100-mesh down.

Two tests were run to compare the permeability numbers of sharp and smooth sands of the same mesh. Samples of 20 and 40-mesh sands, sharp and smooth, were carefully prepared and examined for permeability and voids.

	Sharp		Smooth	
	Permeability	Voids	Permeability	Voids
20 mesh.....	18	39.6	25	33.8
40 mesh.....	52	40.0	60	34.8

These figures indicate that a sharp sand does not pack as readily as a smooth one, resulting in more void space and greater permeability. It is very likely that this results in a weaker core.

Some interesting information was obtained by mixing sands of various

meshes. When 20 volumes of 40-mesh sand having a permeability of 71 were mixed with 80 volumes of 150-mesh sand having a permeability of 600, 96 volumes of sand with a permeability number of 730 were obtained. In another test 40 volumes of 20-mesh sand having a permeability of 31 were mixed with 60 volumes of 150-mesh sand having a permeability 660; the mixture had a permeability of 974. Both tests indicate that maximum permeability is obtained in sands composed largely of grains of one mesh and that the addition of coarse sand may actually make the sand less permeable.

The water-column aspirator was also used for determining the permeability of baked cores; Fig. 2 shows the arrangement for holding the test core. *M* is a brass tube, the inside diameter of which decreases from each end toward the middle, *N* is an air cock, *O* the test core, and *P* a rubber stopper for connecting to the top of the aspirator column. The test core is a cylinder about ⅝ in. (1.5 cm.) in diameter and 3 in. (7.6 cm.) long. About one half its length is dipped into molten paraffin and quickly removed; this covers the surface with a tight fitting coat without permitting the hot paraffin to penetrate the core. The end is then cleaned with a sharp knife and fitted snugly into the brass cylinder which is then inverted and quickly dipped into the molten paraffin so as to cover the rest of the core and seal the joint at *R*. With the cock *N* open the cylinder is now fitted on the water column, the cock *N* is closed, and cock *F* is opened. If the water drops slightly and then comes to a standstill, the joints are tight and the core is sealed. The cock *F* is now closed and the upper end of the core carefully opened with a knife. After adjusting to the mark *H* the time required for the water level to fall from *H* to *K*, Fig. 1, is measured as in the sand tests.

The method described gives a comparative measurement of the permeability of cores made with various binders and various sands. With it, we have found that the following relation exists roughly between the permeability of a sand and the resulting core when linseed oil is used as the binder, ratio 40:1.

Permeability of Sand	Permeability of Core About	Permeability of Sand	Permeability of Core About
1000	35	5000	160
2000	70	6000	190
3000	100	7000	220
4000	130		

Gas Content

By the term gas content is meant the quantity of gas that a core of given size will give off on being heated to the temperature of the casting. It does not include the gas given off in the process of baking but only that which comes off in the casting and which must be allowed to escape

through vents. Our method of measurement has been a purely gravimetric one and consists merely in determining the per cent. loss of weight when a core is heated to about 1400° C. in an electric furnace. This temperature was determined by pouring a casting around a core in which a pyrometer point was embedded, the size of core and casting being about an average for the work we are doing in our foundry. After it has cooled, the burned core from the test is examined with regard to fragility—it should crumble easily between the fingers, otherwise the binder is not properly burned out and such cores are apt to be troublesome on the knockout bench.

We have compared a number of commercial core oils with straight linseed as regards gas content and find that most of them run considerably higher. Straight linseed oil mixed 1 to 40 with a sand of about 1000 permeability should produce a core of less than 1 per cent. gas content; a number of oils, in similar mixtures, showed a gas content of over 2 per cent. One of these oils was carried through the foundry on a test run, the cores were used in a valve body very prone to blow and compared with an equal number made from straight linseed oil. Of the linseed cores, no blows were obtained while 2.4 per cent. of the test cores resulted in blows.

Strength

It is sometimes desirable to express the strength of green cores in figures for the sake of comparing bonds of various sands or for checking on the uniformity of mixing conditions. For such purpose a sample core 1 in. (2.54 cm.) square in cross-section and 10 or 12 in. in length is made in a core box especially for the purpose, ramming it as uniformly as possible; this core is then carefully pushed lengthwise over the edge of the table until it breaks. The length broken off by its own weight is taken as the measure of its strength; an average of three or four tests is usually taken. This figure depends not only on the bond of the sand but also on the binder and water used. To work well and handle without excessive breakage, sand should show a "green strength" figure of 1.5 in. or better.

A Wadsworth core-testing machine is used in Ohio Brass laboratory for determining the tensile strength of baked cores. The test cores have a cross section of 1 sq. in. Five determinations are usually averaged.

Other Tests Made

In order to determine the resistance that a core or core binder offers to moisture a sample is soaked in water for 24 hr. and then examined for softness. Of course, water-soluble binders, such as molasses, glutein, dextrin, etc., dissolve entirely under such treatment: this test is used only in the comparison of commercial oil binders.

Another laboratory test that is of considerable value in comparing oil binders and in checking on the uniformity of a product is the determination of the iodine absorption number. This measures the sticking power of an oil and hence is a fair index to its value in core making. Straight linseed oil shows an iodine number of about 170. An oil of low iodine value, say in the neighborhood of 100, usually produces a weak core.

In any of the foregoing tests, it is well to start with thoroughly dry sand, otherwise there is more or less guesswork about the volume and the moisture content. For a given amount of tamping or shaking, sand increases in volume almost 20 per cent. as the moisture content increases up to the saturation point.

Conclusion

The foregoing tests cover the field fairly well and give a fair index to the value of a sand, core, or binder. They have been most useful to us in compounding core-sand mixtures for particular purposes and in selecting sands and binders from those on the market. As stated, the results of these tests are not accepted as conclusive and large orders placed, based on them alone. When a sand or binder shows up well in the laboratory, it is given a trial run in the foundry and the results carefully observed. Nor are all these tests run on each sample submitted. A few of the more indicative tests, such as visual examination, fineness and permeability for sands, and strength and gas content for binders, usually show whether it is worth while to carry the investigation further.

In all tests, the aim is to compare the sample with a standard with which we are familiar. A number of commercial binders and two or three mixtures compounded in our own plant have been tried out with only partial success; the best results have been obtained with straight linseed oil, which is now used as the standard with which other binders are compared.

This paper is not offered as the final word on the subject of cores and methods of testing. We believe, however, that the methods outlined and the results obtained are worthy of consideration in that they are a step toward a more systematic investigation of the subject than has been attempted heretofore.

DISCUSSION

A. A. Grubb.— In testing samples we used only dry sand. We mixed the sand with linseed oil for one set of test pieces and the sand with the sample under test for the other and made the cores as nearly alike as possible; in other words, we tried to make every condition as uniform as possible and baked the cores side by side in the oven. We have found that more uniform results are obtained by starting with the dry sand.

F. A. SCHUTZ, Decatur, Ill.—There is nothing better than linseed oil. Dry sand should be used because the oil will mix a great deal better in it than in a sand slightly damp. We dry all our sand.

ALFRED C. LANE,* Cambridge, Mass. (written discussion).—This paper confirms, in a general way, the results obtained by Ries and Rosen.[1] It would be interesting if the authors would compute the quality factor (average fineness × ratio of air flow rate) to determine if it is a reliable indication of the relative desirability of sand within a given group.

H. B. SLEETH, Wilmerding, Pa.—Why do some Lake Erie sands require 60 per cent. more oil than some Lake Michigan sands? Is it due to a difference in the grains?

A. A. GRUBB.—We have had little experience along that line until within the last few weeks, when we have found the same condition. Under the microscope the grain of the sand that requires the more oil, or binder, seems to be coated with a dark film, which, I think, absorbs the binder; on the fineness test, the difference does not show up.

F. A. SCHUTZ.—The difference in sands can be told when mixing them. A sharp clean sand that requires comparatively little oil will leave the hands clean.

H. B. SLEETH.—I do not agree with that, because crushed sandstone has no clay but it requires much more oil to give it the same strength as the Lake Michigan sand. Lake Erie sand requires the same amount of oil as crushed sandstone.

A. A. GRUBB.—Is it not true also that quite often sandstone contains more partly decayed stone than does a good silica sand like Lake Michigan sand? In that case the decayed rock would certainly absorb more oil that a hard silica.

H. B. SLEETH.—I think the difference in absorption is due to the shape of the grain; I think that the round grains absorb less oil than the angular grain.

G. H. CLAMER,† Philadelphia, Pa.—May not the trouble be due to the porosity of the grain rather than to the form? Some grains are more porous and therefore will absorb more oil than others, and therefore require more bonding oil.

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* Professor of Geology, Tufts College.

[1] Michigan Survey (1907) 60.

† Vice-president, Ajax Metal Co.

A. A. GRUBB.—To test a baked core, we make two test pieces, one, similar to the briquette used for cement testing, is broken in a Wadsworth core-testing machine and used as a measure of the relative strengths of binders (when the same sands are used) and for the relative strengths of the sands (when the same binder is used). The other test piece is a cylinder, $\frac{5}{8}$ in. in diameter and 3 in. long, which is used in the permeability test. In order to draw the air through the length of the core, this cylinder is immersed in molten paraffine slightly above the melting point, so that practically none is absorbed by the core; the ends of the core are then cleaned and one end is fitted into a small brass cylinder, that fits on the top of the aspirator column. The time required for the water level to fall from one mark to the other, in seconds, is taken as the measure of the permeability of the core; the larger that number, the closer is the core.

Coke and Byproducts as Fuels for Metals Melting

By F. W. Sperr, Jr.,* Pittsburgh, Pa.

(Columbus Meeting, October, 1920)

The byproduct coke oven is the most important artificial source of fuels for metals melting. Its products are solid, liquid, and gaseous in form. The amount of coke and primary byproducts obtained per ton of coal varies with the nature of the coal. The following represents the results obtained in many plants:

Metallurgical coke (over ¾ in.)	69 per cent. of coal
Domestic coke (½ to ¾ in.)	2 per cent. of coal
Breeze (under ½ in.)	4 per cent. of coal
Surplus gas, cubic feet per net ton	6600
Gas for heating ovens, cubic feet per net ton	4400
Tar, gallons per net ton	9
Ammonium sulfate, pounds per net ton	25
Benzols, gallons per net ton	4

All of these products, except ammonium sulfate, have important fuel value. Part or all of the metallurgical coke may be crushed or screened to furnish additional domestic coke. If producer gas is used, there will be a surplus of 11,000 cu. ft. of coke-oven gas per net ton of coal.

The use of coke in the metallurgical industries has been retarded by the mental attitude of writers who disregard the dependence of coke quality on the conditions of its manufacture. Terms like "byproduct coke," "beehive coke," "48-hour coke," and "72-hour coke" are only generally descriptive and tell nothing of the coke quality. For example, one writer[1] stated that in brass-foundry practice, Connellsville coke is considered much superior to byproduct coke on account of the high sulfur content of the latter. Another[2] says, "At equal prices for hard Connellsville coke and for byproduct coke at the foundry door, the hard coke is unquestionably cheaper. It will melt more metal per ton than the byproduct coke and requires less labor, as the byproduct coke is less dense and burns faster, thus requiring more frequent firing." A little study of the conditions under which coke is manufactured will show the error in making general statements like these. The percentage of sulfur in coke depends largely on that in the original coal, and byproduct coke from a

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[1] W. R. Dean, Metal Ind., vol. 8, p. 461.

[2] U. S. Bureau of Mines *Bull.* 73.

given coal will have a little less sulfur than beehive coke made from the same coal. The density and rate of burning of byproduct coke depend on the coal mixture and its preparation and on the design and operating conditions of the oven. Any properly equipped plant can easily produce coke harder and denser than Connellsville beehive coke if it is desired.

The modern byproduct coke oven has remarkable flexibility of adjustment combined with constancy of operation. Temperature conditions are controlled with such fine precision that the ovens are pushed and charged with clockwork regularity. Modern plants have run for years without losing more than a few minutes of their original schedule.

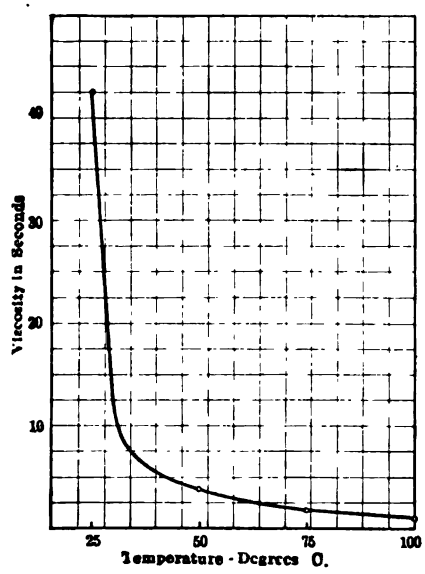

FIG. 1.

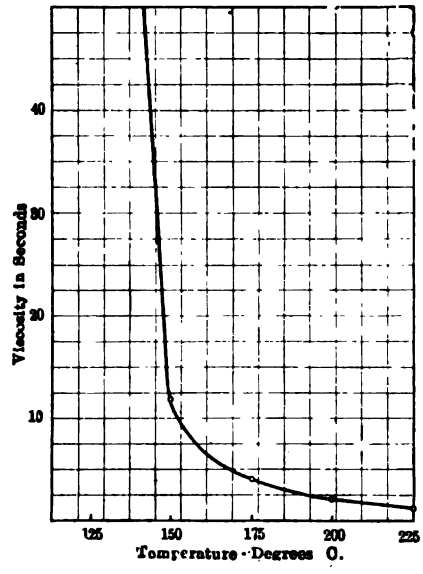

FIG. 2.

FIG. 1.—VISCOSITY OF COKE-OVEN TAR, BY STORMER VISCOSIMETER, IN SECONDS PER 50 REVOLUTIONS.

FIG. 2.—VISCOSITY OF COKE-OVEN PITCH (ABOVE 350° C., 63.1 PER CENT.), BY STORMER VISCOSIMETER, IN SECONDS PER 50 REVOLUTIONS.

The control of coke quality by the use of different kinds of coal, by the method of preparing the coal, and by the regulation of conditions under which it is coked are becoming better understood. It is also possible to design ovens that will make coke of excellent quality from coals that were formerly considered unsuitable. As a result, the range of coals that can be successfully coked in the byproduct oven is now far greater than that of coals suitable for beehive coking.

One of the greatest achievements of modern byproduct coking has been to bring the most important elements of coke quality largely under the control of the operator, so that it is possible to produce coke conform-

ing closely to certain specifications. The basis for the specifications depends largely on the needs of the customer, who should have a correct understanding of his own requirements. When a given coke is compared with some other coke or other fuel, complete information regarding its manufacture is necessary. Furthermore, making a single series of tests and comparing the results thus obtained do not by any means exhaust the possibilities.

The principal factors affecting the manufacture of coke are as follows: (1) kind of coal used; (2) preparation of coal (*a*) washing, (*b*) compression, (*c*) pulverization, (*d*) mixing; (3) design of oven; (4) oven temperature; (5) duration of coking; (6) quenching. Each of these factors is, to a large extent, controllable either in the design of the plant or in its operation. The design of the oven depends partly on the kind of coal available.

With the proper selection of coals, coke may be easily made to conform to the chemical specifications usually desired; the physical character is more difficult to control; it depends on each of the factors named. The addition of from 15 to 35 per cent. of Pocahontas or Somerset coals to high volatile coals increases the size and "blockiness" and diminishes the friability of the coke produced.

Even with a restricted source of supply, the possible control over coke quality is great. Washing reduces the percentage of sulfur, ash, and sometimes, incidentally, phosphorus. Compression is largely used in European practice for improving structure, but it has not been found necessary by any plant in this country. Pulverization has considerable effect on size, cell structure, and friability. The size, hardness, friability, and, to some extent, the cell structure are considerably affected by the temperature and duration of coking. The quenching operation affects principally the moisture content. With a practical understanding of the effects of the different variable factors in various combinations, much can be done toward keeping coke at the desired standard.

The results obtained with byproduct coke in the blast furnace are due not only to improvements in coke quality, but to a better understanding of the requirements of the blast furnace and improvements in blast-furnace equipment and operation. It is now generally admitted by blast-furnace men that the ideas prevalent 10 to 15 years ago regarding coke, especially with reference to its physical characteristics, were generally wrong. One of these ideas was that the material must be left in the oven until practically all of the volatile matter was expelled. Experience has shown that, for best results, care must be taken to prevent overcoking; the best practice is to push the ovens a little "green."

It does not follow, however, that the coke which will work best in a certain type of blast furnace with a certain ore mixture is the one best suited for metal melting. In certain operations, of which the blast fur-

nace is typical, it is desirable that the coke burn as rapidly as possible to carbon monoxide. In other operations, of which the iron foundry is typical, the essential thing is combustion to carbon dioxide. The coke must not burn too rapidly, as it will then tend to burn to carbon monoxide which is wasted above the metal. Strength is important in this case. In each case, the elements of size, hardness, and cell structure are interrelated in determining suitability. The ideal coke for the iron foundry should have hardness, strength, heavy cell walls, and uniformity in size. Size and hardness are compensating qualities; the harder the coke, the smaller it may be.

In the melting of non-ferrous metals, oxidation and loss by volatilization are of prime importance; coke consumption is, to some extent, secondary. Coke that would give the best results in a brass melting furnace would probably differ from that considered to be the best for either the iron foundry or the blast furnace. It will have to be decided, in each case, whether the advantage gained from using a special grade of coke or melting non-ferrous metals is not balanced by the increased expense involved in its manufacturing. Some data on various byproduct cokes are given in Table 1.

Tar and Tar Products

The use of coke-oven tar as a metallurgical fuel has grown steadily during the past few years. With the coals commonly used in a number of important plants, the yield is about 9 gal. per ton. It is estimated that 251,000,000 gal. of byproduct coke-oven tar were produced in the United States in 1919; the amount produced this year will, undoubtedly, be much larger.

The characteristics of coke-oven tar vary somewhat with the kind of coal and operating conditions, but the data given in Table 2 are fairly representative. The heating values show that tar is a highly concentrated liquid fuel, its high specific gravity giving it about 10 per cent. more British thermal units per gallon than ordinary fuel oil. Fig. 1 shows the range of viscosity of a representative coke-oven tar from ordinary temperatures up to 100° C.

The most important use of tar as fuel has been in the manufacture of open-hearth steel, where it has largely replaced or supplemented producer gas or fuel oil. The tar is generally atomized with steam; but some plants preheat it a little and use cold air for atomization. About 10 per cent. less tar than fuel oil per ton of steel produced is used under similar conditions. When working with hot metal, with about 25 to 30 per cent. of cold scrap, from 38 to 40 gal. of tar is consumed per ton of steel produced. Tar makes a hotter flame than producer gas and greatly increases the capacity of the furnace. It is to a considerable extent combined with coke-oven gas or producer gas; the proportions depend on the

supply, at some plants the quantity runs as low as 5 gal. per ton. The resulting flame has better melting efficiency than straight gas, apparently due to its higher temperature and better radiating properties. Although tar has been used in Europe in brass-melting furnaces, in the same manner as fuel oil except for preheating, to the writer's knowledge it has not been applied to the melting of non-ferrous metals in America.

Raw tar for use in comparatively small quantities is difficult to obtain at present. It is estimated that an additional 8,000,000 gal. per year could be obtained, if all the beehive ovens now operating were replaced with byproduct ovens. The tar oils produced in the primary distillation of this material have been largely used in Europe, and there is considerable information regarding their successful application for the melting of non-ferrous metals. In America, on account of the demand for these oils by the dye and creosoting industries, they may not be available as fuel for some time. Coal-tar pitch, however, might be used as a metallurgical fuel, if a successful method for applying it could be worked out. Pitch melts readily to a liquid similar to raw coal tar, and there seems to be no reason why, with preheating, it could not be burned in a similar manner. Fig. 2 shows the viscosity curve for a typical medium-grade pitch; other characteristics are given in Table 3.

Coke-oven Gas

The modern byproduct coke oven is not only adapted to the manufacture of metallurgical coke, but is capable of furnishing coal gas equal to that manufactured in the ordinary gas retort. The annual consumption of coke-oven gas for domestic and industrial purposes, outside the iron and steel industry, is practically 40,000,000,000 cu. ft. per year, and the rate of consumption is being rapidly increased. A conservative estimate places the average yield at 10,500 cu. ft. per ton of coal coked; modern practice approaches 11,000 cu. ft. per ton of coal as an average. If all the coke produced in the United States were manufactured in byproduct ovens, the total gas production would exceed 900,000,000,000 cu. ft. per year, which is more than the annual production of natural gas. It is estimated that the actual production of coke-oven gas during the next five years will be at an average rate of 480,000,000,000 cu. ft. per year. Of this, little more than one half will be available for uses other than heating the ovens. The more modern ovens require for the coking operation only 40 per cent. of the heating value contained in the total gas evolved. With the increasing demand for high-grade gas, the tendency is to erect combination ovens, which may be heated with producer gas or blast-furnace gas, thus releasing high-grade coke-oven gas for sale.

With properly selected coals, the modern byproduct coke plant will produce straight gas having a heating value of 560 B.t.u. per cubic foot after the removal of benzols. The present tendency in building coke plants for gas manufacture is to eliminate gas separation.

Table 4 shows typical analyses of coke-oven gas after the removal of hydrogen sulfide. Before purification, it contains from 300 to 700 gr. total sulfur per 100 cu. ft.; from 8 to 15 gr. of this is in combination with carbon, principally as carbon disulfides while the rest is in the form of hydrogen sulfide. The amount of sulfur is considerably less, in proportion to the heating value of the gas, than in the producer gas made from the same coal; and as producer gas is generally made from high-sulfur coals, the difference is even more pronounced. Producer gas also contains a higher proportion of carbon disulfide, which is much more difficult and expensive to remove than hydrogen sulfide. It is questionable whether the removal of hydrogen sulfide from coke-oven gas is ordinarily necessary where the gas is to be used in open-hearth steel furnaces. For general use in metals melting, though, the gas should be purified; this is readily accomplished by the usual iron-oxide process which is well established in the illuminating-gas industry. The cost of purifying is relatively much lower than that of purifying producer gas. The general advantages of high-grade gaseous fuels for metals melting have been frequently discussed. No preheating, recuperation, or regeneration of the gas is necessary; it would be disadvantageous in the case of coke-oven gas, which readily undergoes decomposition when heated. The use of coal gas results in greater ease of regulation, reduced loss of metal, increased speed of heating, and longer life for the furnace. The advantages appear to be greatest in comparison with solid fuels; but there is also some advantage in each respect over oil.

For five years, ending in 1909, the London Mint required 1100 lb. of coke on the average to melt one ton of metal; from 1911 to 1916, it required 12,220 cu. ft. of coal gas. The crucibles lasted approximately one-third longer with gaseous than with coke firing and the labor was about one-fifth less. Following are comparative figures for various metals:

Metals	Approximate Specific Gravity	Approximate Temperature of Pouring, Degrees C.	Cubic Feet of Gas Used per Ton Melted
Gold.....	17.3	1150	7,000
Silver.....	10.35	1090	12,000
Bronze.....	8.9	1165	14,500

All things considered, coke-oven gas is cheaper than any other high-grade artificial gas, and as it is coal gas of low specific gravity, it has a lower cost of distribution per British thermal unit than all other artificial gases whether of low or high grade.

Lower Grade Gases Produced from Coke

Not only is coke the principal fuel used in the manufacture of water gas, but it is an important material for the manufacture of producer gas,

TABLE 2.—*Characteristics of Typical Byproduct Coke-oven Tar*

Moisture, per cent	1.50
Specific gravity (15° C.)	1.165
Pounds per gallon	9.70
Coefficient of expansion per 1° C	0.000588*
British thermal units per pound (gross)	16,200
British thermal units per gallon (gross)	157,140
Flash point, degrees C	90 to 100
Free carbon, per cent	4.00
Sulfur, per cent	0.60
Ash, per cent	0.05
Distillation:	
Light oils (to 170° C.) per cent	0.50
Middle oils (170–270° C.) per cent	19.50
Heavy oils (270–350° C.) per cent	20.00
Pitch, per cent	60.00

*This figure is not to be confused with the specific gravity correction which is 0.000685 per degree C. to be added to or subtracted from the observed specific gravity to obtain the true specific gravity at 15.5° C.

TABLE 3.—*Characteristics of Byproduct Coke-oven Pitch*

Melting point, degrees C	85
Specific gravity (15° C.)	1.25
British thermal units per pound	15,500 to 16,000
Flash point, degrees C	160 to 232
Free carbon, per cent	20 to 25
Fixed carbon, per cent	30 to 35
ULTIMATE ANALYSIS	
Carbon, per cent	92 to 93
Hydrogen, per cent	3 to 5
Nitrogen, per cent	0.6 to 1
Oxygen, per cent	0.0 to 2
Sulfur, per cent	0.5 to 1
Ash, per cent	0.05 to 0.4

TABLE 4.—*Typical Analyses of Gas from Koppers Byproduct Coke Ovens*

	CO_2	Illuminants	O_2	CO	H_2	CH_4	N_2	B.t.u.	Specific Gravity
Straight gas, before removing benzols	2.2	3.5	0.3	6.8	47.3	33.9	6.0	591	0.44
Straight gas, after removing benzols	2.2	2.6	0.3	6.9	47.8	34.2	6.0	562	0.42
Rich gas, before removing benzols	2.6	4.3	0.2	6.3	46.3	35.0	5.3	630	0.45
Rich gas, after removing benzols	2.6	3.2	0.2	6.4	46.8	35.4	5.4	605	0.42
Lean gas, before removing benzols	2.1	2.0	0.3	6.0	57.0	27.0	5.6	528	0.38
Lean gas, after removing benzols	2.1	1.0	0.3	6.1	57.5	27.3	5.7	497	0.35

NOTE.—These analyses are taken from different plants and consequently represent different coals and somewhat different operating conditions.

TABLE 5.—*Properties of Blue Water Gas and Coke Producer Gas*

	Blue Water Gas	Coke Producer Gas
CO_2, per cent	6.2	5.0
O_2, per cent	0.8	0.0
CO, per cent	39.0	23.0
H_2, per cent	49.0	14.0
N_2, per cent	5.0	58.0
British thermal units (gross)	305.0	128.0
British thermal units (net)	278.0	120.0
Specific gravity	0.55	0.87
Flame Temperature:		
Cold air	1920° C.	1495° C.
Preheated air (500° C.)	2110° C.	1650° C.
Air Requirement:		
Cubic feet air required for complete combustion of 1 cu ft. gas	2.17	0.89

Reclamation of Metal from Brass-foundry Refuse

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(Columbus Meeting, October, 1920)

THE reclaiming of metallics from slag and sweepings is of vital interest to every brass-foundry man, but the first cost and interest on the investment often make it prohibitive for the small foundry to enjoy the benefits of a complete concentrating unit. However, the cost of such an installation and the cost of operation are often exaggerated to such an extent that foundries dispose of their copper-bearing refuse at a great loss. This paper gives the actual costs and the returns obtained in the reclaiming plant used at the Ohio Brass Co. This plant is divided into two sections—the preliminary treatment and concentrating departments. In the former occur the screening, crushing, and hand-picking operations whereby most of the non-valuable and heavy metallic constituents are removed. The concentrating equipment consists of an elevator, bins, jigs, ball-mill, and table.

PRELIMINARY TREATMENT

The preliminary treatment varies, depending on whether the material is slag, foundry-floor sweepings, or brass casting-floor sweepings. Material of the first class is produced from the operation of six Steele-Harvey and six Schwartz furnaces; the second class represents sweepings from an average of thirty-five molding floors per day; and the last is collected around the sprue cutters and knockout bench.

Treatment of Slag

The slag, analyzing 30 to 40 per cent. copper, is passed over a 3-mesh yard screen (Tyler standard mesh) stretched on an inclined rectangular frame supported by adjustable legs and equipped with a hopper which directs the undersize into a barrow. The fine product, running about 20 per cent. copper and representing 20 to 25 per cent. of the total slag, goes direct to a storage bin for concentrator feed. The oversize is charged into a No. 2 Hill cinder crusher, which takes 175 to 200 lb. to a charge and crushes two charges per hour through a No. 4 riddle. It

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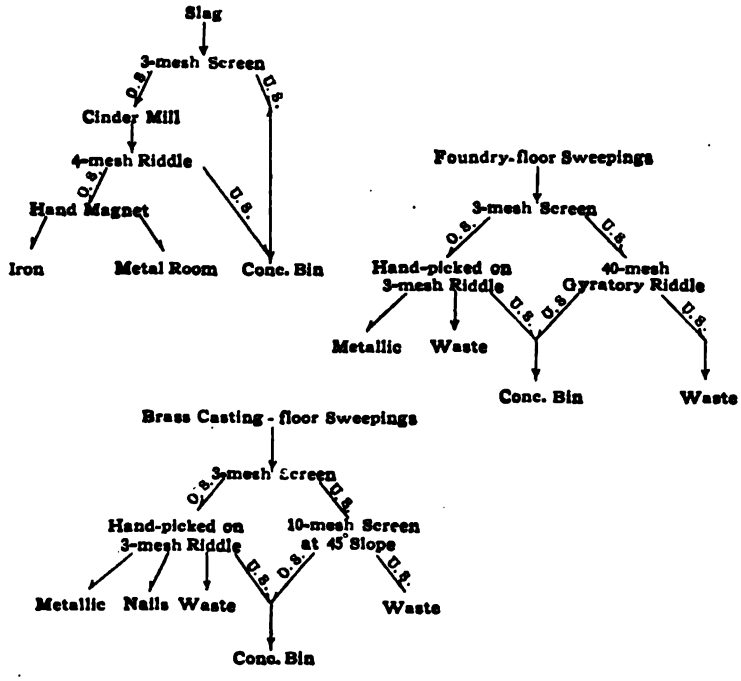
requires 6 hp. and operates at 36 r.p.m. The undersize from the riddle goes to the storage bin and the oversize, after treatment with a hand magnet, to the metal room. At this point, 30 per cent. of the material charged to the crusher is removed as heavy metallic and the fines for concentration treatment carry 20 per cent. copper. These percentages are, of course, subject to change due to the character of the metal charged to the furnace and to the care in skimming. The flow sheet is shown in Fig. 1.

FIG. 1.—FLOW SHEETS FOR PRELIMINARY TREATMENT.



Treatment for Foundry-floor Sweepings

Foundry-floor sweepings consist of heavy metallic, spillings, cores, and sand. The material for hand picking is removed by the 3-mesh screen and represents 20 to 25 per cent. of the total weight. This is hand picked on a 3-mesh riddle for metallic, nails, and waste. The metal recovered is about 5 per cent. of the original sweepings. A small amount of undersize obtained from this riddle is added to the material passing the yard screen. The undersize from the yard screen goes to a Combs gyratory riddle using a 40-mesh screen. Material remaining on the riddle, say 12 per cent. of the total sweepings, averages 30 per cent. copper and is ready for concentration. Material passing this riddle, about 65

per cent. of the total sweepings at 0.30 per cent. copper, goes to the tailings dump. The flow sheet is shown in Fig. 1.

Treatment for Brass Castings-floor Sweepings

Brass castings-floor sweepings contain heavy metallic, light metallic, nails, wires, broken cores, and core sand. This is kept separate from sweepings taken around the grinders, of which the quantity is so small that the treatment will not be discussed. The procedure is quite similar to that in use for sweepings from the foundry. The 3-mesh yard screen removes 20 to 25 per cent. for hand picking and the recovery of metal is the same as from foundry sweepings. A small percentage of nails is also reclaimed. Undersize from this yard screen goes to screen of similar construction, but with a heavy 10-mesh screen, set at an angle of 45°. The coarse material from this, 10 to 15 per cent. of the total sweepings and approximating 5 per cent. copper, is taken to the concentrator bin. The fines, about 65 per cent. of the total sweepings, analyze less than 1 per cent. copper and go to waste. The flow sheet is shown in Fig. 1.

CONCENTRATING DEPARTMENT

In the concentrating department, the feed is charged, by elevator, into a 70 cu. ft. (2 cu. m.) steel feed hopper, the bottom of which is

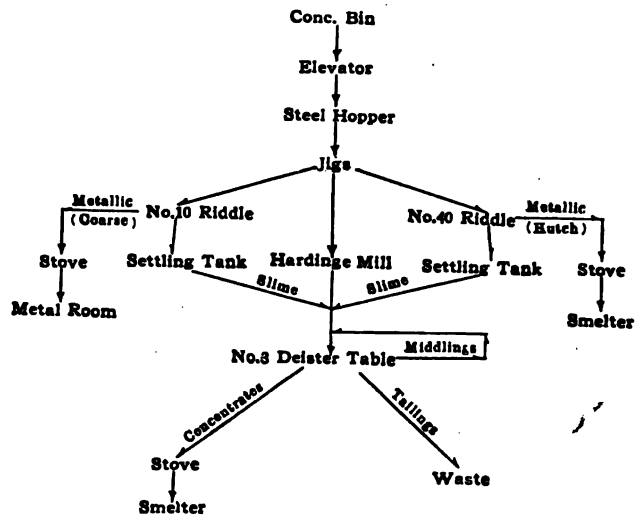


FIG. 2.—FLOW SHEET FOR CONCENTRATING MILL.

equipped with an automatic feeder that will pass such stray foreign substances as wires, nails, or large pieces of slag. This feeds to a two-compartment Woodbury jig classifier, which operates at 200 r.p.m. and is driven by a 5-hp. motor. The first compartment, 12 by 21 in. (30.5

by 53.3 cm.) has a 10-mesh screen and a 1⅜-in. (3.5-cm.) stroke. The second compartment, 18 by 24 in., has a 6-mesh screen and a ¾-in. (1.9-cm.) stroke. The classifier requires from 40 to 50 gal. (151 to 189 l.) of water per minute; 17 gal. go over the tail board to the table and the balance is discharged with the concentrate. Both jigs discharge a fine, or hutch, concentrate, which passes through the screens and downward against the water pulsations. The hutches, after being discharged from the machines, are combined and carried by launder to a 40-mesh riddle set over a settling tank. The coarse concentrate, discharged from above the screen on the second compartment, is caught on a 10-mesh riddle set over the same tank. A man stationed at this point changes and cleans the riddles at frequent intervals. By this method, all fines are washed out and a clean high-grade metallic is secured. A small amount of slime rich in metal is recovered from the settling tanks and hand-fed to the Deister table. The water overflowing from this tank is carried to the main sump. The water passing over the tail board goes to the table and then to the sump. The latter serves the double purpose of settling tank and reservoir, a small centrifugal sand pump being used to return the water to the machines.

The metallic recovered in the form of coarse jig concentrates, after drying and passing over a Dings M–2 separator, is taken direct to the metal room for re-use. It is almost pure and represents 60 to 70 per cent. of the total metallic in the feed. The hutch concentrate shows 65 to 70 per cent. copper and carries about 20 per cent. of the metallic in the feed. It is dried and sold.

The tails from the second jig are conducted into a scoop feeder on a 3 ft. by 9 in. Hardinge ball-mill. This feeder carries a heavy 14-mesh screen and all feed passing is by-passed around the mill and joins the discharge. The mill is loaded with 500 lb. of chrome-steel balls, maximum size 2½ in. It operates at 36 r.p.m. and requires about 6 hp. All discharged material is crushed to 60 mesh or finer.

The fine pulp is conveyed by launder to a No. 3 Deister slime table. The copper content is from 4 to 5 per cent. or say 13 per cent. of the total metallic in the feed. Three products are made: *i.e.*, concentrate, middlings, and tailings. When a regular run is completed, the table is readjusted and the middlings refed at the head end. The middlings then produced are classed and thrown out with the tailings. The table, itself, has been re-riffled. The arrangement was retained but the present riffles are double the thickness of the original ones. It is operated at 260 r.p.m. with a ½-in. stroke and requires ½ hp. The consistency of the feed is 20 to 25 per cent. solids. The water for the table comes from the jigs and through the Hardinge mill. The amount can be controlled by opening or closing the apertures for hutch and coarse concentrate discharge. The small amount of makeup water required by the system—

2 to 3 gal. per minute—is supplied as wash water for concentrate and middlings. These, as well as the tailings, are caught in large tanks, the water overflowing from the concentrate to the middings to the tailings tanks, thence to the main sump for re-use. When the table is used alone, water is supplied through a by-pass. Concentrate as rich as 65 per cent. copper can be produced, but it has been found advisable to hold it to between 40 and 50 per cent. copper. With a 45 per cent. concentrate, the tailings will carry 0.7 to 0.9 per cent. copper, which is equivalent to a loss of approximately 1 to 2 per cent. of the total metallic fed to the mill. Screen tests have shown that 60 per cent. of this loss is in the form of metallic finer than 150 mesh. The concentrates are dried and sold on the copper content basis.

All drying is done in a sheet-iron oven 30 by 30 by 72 in. (76.2 by 76.2 by 182.8 cm.). This holds twelve trays, each 24 by 30 by 2 in., so set that the heat travels under and over each one. Gas is used for fuel and the burners are two extra heavy 2-in. (5-cm.) perforated pipes. The capacity of this oven is 1500 lb. (680 kg.) of heavy concentrates per charge and 6 to 8 hr. are required to dry this amount.

TABLE 1 .—*Quantities and Analyses*

		Per Cent. by Weight	Copper Content, Per Cent.
Foundry-floor Sweepings	Recovery: Metallic	6.0	
	Jig feed, 3 to 40 mesh	12.0	20.0 to 30.0
	Jig feed from hand picking	5.5	20.0
	Reject: Cores	11.5	
	Fines through 40 mesh	65.0	0.2–0.7
	Production: 100 lb. per day per molding floor.		
Brass Castings-floor Sweepings	Recovery: Metallic	5.0	
	Jig feed, 3 to 10 mesh at 45°	11.0	5 to 10
	Jig feed from hand picking	9.0	10 to 15.0
	Nails	1.0	
	Reject: Cores	5.0	
	Wire	3.0	
	Fines through 10 mesh at 45°	66.0	0.5–1.0
	Production: 1500 to 1700 lb. per day.		
Foundry Slag	Undersize from 3 mesh	23	20.0
	Undersize from 4 mesh after crushing	54	15.0 to 20.0
	Metallic recovered after crushing	23	75.0 to 85.0
	Production: Steele-Harvey, 50 lb. slag per ton metal melted.		
	Schwartz, 142 lb. slag per ton metal melted.		
Concentrating	Heads		20.0 to 25.0
	Tailings	68	0.7 to 0.9
	Jig hutch	8	60.0 to 70.0
	Jig concentrate	18	70.0 to 80.0
	Table feed		40.0 to 5.0
	Table concentrate	6	40.0 to 50.0

The Dings magnetic separator is used principally for borings and chips from the machine shop; the washings from the jigs constitute a very small percentage of its burden.

Estimated Cost of a Complete Reclaiming Plant and Other Data

The following costs must be accepted only as approximations on account of the rapidly changing market. Furthermore, erection costs as well as housing, overhead, and upkeep are not mentioned because they would vary greatly in individual plants and locations.

For Preliminary Treatment		For Concentration	
Gyratory riddle	$150.00	Elevator and bin	$2000.00
Yard screens (2)	50.00	Woodbury jigs	800.00
Hill cinder crusher	450.00	Hardinge mill	1200.00
Barrows, riddles, etc	100.00	Deister slime table	500.00
Total	$750.00	Pump	300.00
		Tanks	200.00
		Drying stove	200.00
		Total	$5200.00
		Total plant	$5950.00

Data on Operating Labor and Power

Preliminary Treatment

Screening slag over a 3-mesh yard screen	1 ton per man-hour
Screening sweepings over yard screens	1 ton per 1½ man-hour.
Riddling sweepings on a 40-mesh gyratory	1 ton per 2½ man-hour.
Hand picking	1 ton per 15 man-hour.
Cinder-mill labor	1 ton per 6 man-hour.
Cinder-mill power	1 ton per 27 kw.-hr.

Concentrating

Labor: Elevator	1 ton per man-hour.
Miscellaneous	1 ton per 9 man-hour.

Power: Elevator, 3 hp.; jigs, 5 hp.; ball-mill, 6 hp; table, ½ hp.; pump, 2 hp.; magnetic separator, 1 hp.; gyratory riddle, ⅙ hp.

Proposed Changes

Several important changes are contemplated in the foregoing equipment. These will be directed toward increasing capacity, decreasing labor and power, and gaining a more uniformly sized feed for jigs and tables. It is proposed to place a ⅜-in. (9.5-mm.) mesh screen on the driving end of the Hill cinder crusher. Inasmuch as the finer material is displaced by the heavier and works to the top, the mill can be charged continuously for 3 or 4 hr., or until the accumulation of heavy metallic interferes with the operation. The fines will be discharged continuously through the screen and into the elevator boot. Experimental tests have indicated that the capacity of the mill will be doubled and possibly tripled. This is in great contrast to the present method of operation, where the charge must be completely emptied every half hour, hand-riddled, and then hand-fed to the elevator.

Another proposed change is to have the elevator discharge on to a Dings magnetic pulley, thence on to an impact screen. The sized products from this screen will go to separate bins, one for coarse, or jig, feed, the other for fine, or table, feed. The advantage of this arrangement would be the extraction of all nails, wires, and tramp iron before the feed gets to the concentrating machines and the elimination of fines from the jigs. This should result in an improved grade of fine and coarse concentrate and a decrease in labor and power. A device is also under consideration for dewatering and discharging the jig concentrates into a barrow.

The removal of tailings from the settling tank is extremely laborious work, inasmuch as they are sticky and pack tightly. A scoop conveyor or a dewatering cone with a sand pump have been suggested for this purpose.

A Representative Run

The complete records of a representative run are given herewith. All slag, foundry-floor sweepings, and brass castings-floor sweepings produced in a week were segregated and full data recorded on their treatment. In this period, 750 lb. (340 kg.) of slag were produced from the melting of 30,000 lb. of metal in six Steele-Harvey furnaces, and 7916 lb. from the melting of 112,000 lb. of metal were melted in six Schwartz furnaces. These slags, when combined, carried 38 per cent. copper. The subsequent method of treatment has been outlined in the foregoing. There were 21,600 lb. of foundry sweepings, the clean-up from an average of thirty-five molding floors per day. The brass-castings sweepings, 10,000 lb., were representative of the clean-up after handling small valve and railway castings poured from 71 tons of metal.

Preliminary Treatment on Slag

	Pounds	
From melting 56 tons in Schwartz furnaces, slag and skimmings	7916	
From melting 15 tons in Steele-Harveys, slag and skimmings	750	
Total slag from 71 tons melted	8666	
Undersize through 3-mesh yard screen	1993	
Oversize to cinder mill	6673	
Metallic recovered after crushing	1967	
Balance through No. 4 riddle	4706	
Undersize from yard screen	1993	
Feed for concentrator	6699	
Costs: Screening in yard, 4.5 man-hours, at 55c		$ 2.48
Cinder mill, 20.5 man-hours, 55c		11.27
Labor, 25.0 man-hours		13.75
Power, 89 kw.-hr.		1.78
Flat cost		15.53
Credit on metallic returned to the metal room, 1967 lb. at 17c		$334.39

PRELIMINARY TREATMENT OF FOUNDRY SWEEPINGS

		Pounds
Recovery: Metallic		1,296
Concentrator feed		3,770
Rejects: Cores		2,484
Fines through 40-mesh		14,050
Total weight		21,600
Costs: Screening over 3-mesh, 16.5 man-hours at 55c	$ 9.07	
Riddling over gyratory, 22.0 man-hours at 55 c	12.10	
Hand picking, 36.0 man-hours at 55 c	19.80	
Labor, 74.5 man-hours	40.97	
Power, 3 kw-hr	0.06	
Flat cost	41.03	
Credit on metallic returned to metal room, 1296 lb. at 17c	$220.32	

PRELIMINARY TREATMENT ON BRASS CASTINGS-FLOOR SWEEPINGS

		Pounds
Recovery: Metallic		440
Concentrator feed		2,000
Nails		130
Rejects: Cores		410
Wire		400
Fines		6,620
Total weight		10,000
Costs: Screening over 3 mesh, 7.5 man-hours, at 55c	$ 4.12	
Screening over 10 mesh, 6.0 man-hours, at 55c	3.30	
Hand picking, 19.5 man-hours, at 55c	10.73	
Labor, 33.0 man-hours	18.15	
Power	None	
Flat cost	18.15	
Credit on metallic returned to metal room, 440 lb. at 17c	$74.80	

CONCENTRATING TREATMENT

	Pounds	Pounds Copper
Feed: From slag	6,699	
From foundry sweepings	3,770	
From brass castings sweeps	2,000	
Total feed	12,469	
At 23.6 per cent. copper this equals 2943 lb. copper.		
Recovery: Jig hutch (fine), 912 lb at 65.75 per cent. copper		600
Jig concentrate, 2300 lb. at 85.00 per cent. copper		1,955
Table concentrate, 743 lb. at 42.00 per cent. copper		312
Loss: Tailings from table, 8514 lb. at 0.90 per cent. copper		76
Accounted for, 12,469 lb. at 23.6 per cent. copper		2,943

	Hours
Running time: Elevator	5
Jigs, ball-mill, and table	8
Ball-mill and table alone	3
Drying stove	24
Magnetic separator	3

Costs: Elevator, 5 man-hours at 55c	$ 2.75
Feed, 12 man-hours at 55c	6.60
Failings, 11 man-hours at 55c	6.05
Concentrates, 22 man-hours at 55c	12.10
Miscellaneous, 10 man-hours at 55c	5.50
Labor, 60 man-hours	33.00
Power: Elevator	0.24
Jigs	0.60
Ball-mill	1.00
Table	0.16
Pump	0.32
Magnetic separator	0.04
Flat cost	$35.36

Credit on coarse jig concentrate returned to metal room, 2300 lb. at 17c., $391.00.

Credit on fine jig concentrate to market, 912 lb. (600 lb. copper at 18.5 c. less 4c. smelting charge, $87.00.

Credit on table concentrate to market, 743 lb. (312 lb. copper at 14.5 c., $45.24.

Total return on concentrates, $523.24.

Conclusion

The foregoing shows that the returns on a plant of this type are far in excess of the costs, even after such items as overhead, depreciation, interest, rent, upkeep, etc. have been properly charged. This end is attained primarily through the removal of the large burden of low-grade material by cheap screening methods and the consequent decrease in quantity of material to undergo concentration. Furthermore, the operation of such a plant, once installed and properly organized, is extremely simple. Any intelligent man can be taught, in a few days, to supervise the operations and care for the general mechanical adjustments; but a man familiar with concentrating machinery should frequently inspect the machines, supervise the special adjustments, and watch the routine as well as character of the feed and products.

The same equipment could, no doubt, be used to advantage in a foundry of much smaller capacity. But the small foundry that cannot afford a complete installation should give the copper-bearing material the preliminary treatment, to remove the excess of low-grade material and reclaim all heavy copper. The high-grade fines, about 20 per cent. copper, may then be sold to a concentrating or smelting plant. Another plan would be to crush to a fine pulp in the cinder mill all values recovered by preliminary treatment.

Two charges of foundry slag, each of approximately 300 lb., were crushed in the cinder mill for 90 min. and the product screened over 4, 8, and 20-mesh riddles.

On 4 mesh, 77 lb. contained 77 lb. metallic.
On 8 mesh, 42 lb. contained 42 lb. metallic.
On 20 mesh, 48 lb. contained 41 lb. metallic.
Through 20 mesh, 395 lb. contained 89 lb. metallic.
Total, 562 lb. contained 256 lb. metallic.
Metallic in slag, 45.5 per cent.

Practically all slag in a 300-lb. charge can be crushed to pass a 0.050-in. opening at a cost of 50 to 75 c. The metallic above this size may be recovered by screening and the product passing the screen may be treated in a series of hydraulic trough classifiers. This method should yield a recovery of 90 to 95 per cent. of the total metallic, as against 98 to 99 per cent. when using a jig and table.

DISCUSSION

J. L. JONES,* East Pittsburgh, Pa. (written discussion).—The fact that such a large proportion of foundry and castings-floor sweepings can be reduced to under 1 per cent. copper content by merely screening is of special interest. It means that these sweepings can be concentrated over 50 per cent. without any other equipment than a 40-mesh screen.

The amount of slag given as produced by each Schwartz furnace, 142 lb. per ton of metal melted, seems excessive; our Schwartz furnaces produce 84 lb. of slag per ton. Possibly the high figure is caused by fine grindings or turnings being included in the charge. Where the tonnage of such material is sufficient, the establishment of a smelting department would mean cleaner castings and less loss in machining.

The copper content of 1 per cent. or less for the tailings can be maintained only by careful supervision of the entire process. The tailings in the average plant will run over rather than under this amount. While 1 per cent. of copper, or 20 lb. to the ton, may not repay the labor spent to reclaim it in isolated brass foundries, if central reclaiming plants, which are possible in large cities, were installed, tailings running 1 per cent. copper could be easily treated with profit. In this connection, the various leaching processes should be of interest, especially the ammonia leaching process, because this gives a very pure copper oxide. Lawrence Eddy gives the cost of leaching 450 tons of mill tailings per 24 hr. as 84.9 c. per ton. The ore ran 0.85 per cent. of copper and the waste from it 0.17 per cent. copper.[1]

* Metallurgist, Westinghouse Elec. & Mfg. Co.

[1] Practical Considerations in Ammonia Leaching of Copper-bearing Ores. *Chem. & Met. Eng.* (Apr. 1, 1919) 328–334.

A reclaiming plant equipped for ammonia leaching, or some other leaching process, might be commercially possible if it were conveniently located in a large brass-foundry center. The refuse sand might also be used for building purposes.

G. E. ALDERSON.—Metallic returned to the foundry is valued at the market quotations on metal contained. Material for shipment is valued on the copper content at from four to five cents per pound under New York quotations.

G. H. CLAMER,* Philadelphia, Pa.—We have had quite an elaborate concentrating equipment during the past 10 or 15 years but prior to the war we realized that we were not getting the recoveries we should as our tailing losses were quite high. Investigation showed that a fairly large percentage of the metal content of the tailings was in the form of oxide. It is practically impossible to recover the oxides by any concentrating method. We investigated the ammonia leaching process, because with the ammonia leaching it is possible to recover not only the copper oxide but also the zinc oxide. I am not certain that an installation of that kind would be a commercial success. Its cost is fairly great, because air-tight tanks are required. We are now remodeling our plant. Prior to the war, it was estimated that this remodeling would cost about $40,000; now we find it will cost $100,000. The efficiency of any concentrating plant will depend almost entirely on the amount of money spent, and when considering the expenditure for the installation it is necessary to consider the tonnage that can be put through it. The cost of the equipment must be balanced against tonnage put through and the recovery that will be made.

The paper of Messrs. Wolf and Alderson is the most practical one on the subject that I have heard. It gives actual figures that I know are very nearly correct. The authors make no extravagant claims regarding metal recovery, but the recovery is good.

E. E. THUM,† New York, N. Y.—Foundrymen may not realize that the bulk of copper comes from very low-grade ores. Metallurgical engineers have found that sulfides are fairly easy to concentrate by gravity methods or by flotation. But oxides do not concentrate very well though they may be leached by several solutions. For a central plant handling 1 per cent. oxidized tailings such as Mr. Jones suggests, to be a commercial success, a large amount of uniform material must be handled. Leaching plants in the west daily handle thousands of tons of ore each. I would not want to infer, however, that a smaller installation

* Vice-president, Ajax Metal Co.
† Associate Editor, *Chem. & Met. Eng.*

could not be a success, but to be a success it would have to receive the sweepings of a great many foundries.

O. J. MOUSSETTE, New York, N. Y. (written discussion).—The plan described is elaborate and costly. Clean metal may be obtained at a reclaiming cost of one cent a pound, with an equipment that costs only one-fourth as much to install. The preliminary treatment of the slag, etc. may be eliminated entirely by feeding the foundry refuse material directly into a monarch cinder mill. As soon as it is separated from the slag, the coarse metal passes on to the screen with the fines; thence to a conveyor belt to be hand picked. The material that passes through the ⅜- and ¼-in. screen is conveyed to the Deister concentrating table.

An installation of medium size will average three tons per hour and will require 2¼ hp., which is distributed as follows: No. 2 cinder mill, 1¼ hp.; Deister junior table, ½ hp.; conveyer belt, ½ hp. The estimated cost of installation is $1275, divided as follows: No. 2 cinder mill, $750; junior Deister concentrating table $325; and conveyer belt for hand picking, $200.

G. E. ALDERSON (author's reply to discussion).—An ammonia leaching installation for tailings would be effective but tonnage plays an important part and, furthermore, it would require more floor space and supervision than the average industrial plant can afford. In an ore concentration mill, it is common practice to regrind the middlings and oftentimes the tailings from the first or roughing table and pass them over another table or suitable concentrating device. The regrinding liberates entrained particles of value. This practice could also be utilized in foundry reclamation, the grinding operation being replaced by a trommel or impact screen because we are dealing for the most part (*i.e.*, when under 60 mesh) with free metallic. On any table separation, the divide between concentrates and middlings shows fine metallic coming out with coarse sand. The method suggested would be to pass the pulp over a sand table, the tailings and middlings from this through a trommel with a mesh slightly larger than the fine metallic concentrating out, and the undersize from the screen to a slime table. The coarse discharge might be either recrushed or discarded depending upon metallic content. Such an addition would require about 1 hp. but no additional labor.

Investigation of Brass Foundry Fluxes

By C. W. Hill,* Ph. D., T. P. Thomas,† W. B. Vietz,‡ Pittsburgh, Pa.

(Columbus Meeting, October, 1920)

Fluxes, in general, may be classified according to their use as soldering, foundry or casting, and metallurgical and the chemistry of their action follows quite closely this division. The term foundry or casting fluxes, as used here, refers to the substances added to molten metals, preparatory to casting into molds or ingots, with the object of removing small amounts of impurities that have been introduced in handling or melting the metal, which was placed in a fair state of purity by the previous refining or metallurgical processes. The sources of these impurities are the oxide coating on the surface of the ingots, material extracted or mechanically removed from the crucible or furnace wall, and those formed by the reaction of the molten metal with the heating gases or furnace atmosphere.

As commonly used, the term fluxes is applied to such materials as ammonium chloride, zinc chloride, salt, borax, and boric oxide. A second class of materials, usually called deoxidizers, includes substances such as metallic phosphides, sub-oxides, carbides, and borides, that reduce the metallic oxides present in the metal. A third class includes various compounds that are molten and non-volatile at the temperature of the molten metal and are used primarily to protect the surface of the metal from the action of the furnace or exterior atmosphere; to this class belong such mixtures as lime and fluorspar, lime and soda ash, various minerals, etc. In some cases these protective layers may act in a manner similar to the metallurgical fluxes and dissolve or unite with the oxide impurities of the metal, but as generally employed this latter action is negligible since there is little opportunity for the coverings to come into contact with more than the surface of the metal, and hence they are without action on the body of the molten mass.

The use of fluxes is the result of factory experience and tradition, but an extensive study has not been made of the chemical and physical actions that occur or the effects of these actions on the properties of the metal. It would seem necessary in any successful study of metal fluxes to determine not only what impurities are present in metals melted under

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commercial conditions, but the amount of these impurities. On account of the variety of metals used and their varying degrees of chemical activity, it will be necessary to consider the specific characteristics of each metal and its impurities as well as the properties that it has in common with the others. Thus, some metals are not only oxidized on melting, but have the property of dissolving their oxides. On solidifying, silver rejects the oxygen it has dissolved while molten, but copper does not. The extent to which aluminum will dissolve its oxide was unknown until the work of Rhodin.[1] The experiments made by the authors tend to confirm these results.

It is necessary to bear in mind the operating conditions, as in many cases impurities are not introduced in amounts at all approaching those possible by complete saturation, while in other instances the maximum is usually attained. The nature of the containing vessel and the time during which the hot metal is in contact with the container must also be considered. In general the impurities may be classified, as to source and kind, in the following manner:

Source	Nature of Impurities
From crucible	Combined or dissolved elements:
	Silicon, iron, carbon
	Suspended matter:
	Oxides from crucible as SiO_2
From atmosphere	Oxides-nitrides:
	Dissolved
	Suspended
	On surface of metal
	Dissolved gases:
	Hydrogen, carbon monoxide
	Nitrogen, carbon dioxide, sulfur dioxide
	Water vapor

The properties of molten metal that may be influenced by these impurities are the melting point, surface tension, viscosity, amount of dissolved gases, and strength of the surface film. The properties of the cast piece that may be influenced are the mechanical strength, hardness, electrical conductivity, specific gravity, and coefficient of thermal expansion. The properties of the cast piece will be influenced by the properties of the molten metal when these properties concern the mechanics of molding.

The chemistry of soldering and metallurgical fluxing is well known, as is that relating to the action of deoxidizers in foundry fluxes. The chemical reactions of the ordinary fluxes, such as the volatile chlorides of ammonium and zinc, are not understood, and there is some question as

[1] *Trans.* Faraday Soc. (1919) **14**, 134.

to the extent of the chemical reaction, since it has been possible, apparently, to duplicate the action of these fluxes by mechanical means alone.

Physical Changes Caused by Fluxes

The physical changes caused by the small amount of such fluxes as zinc chloride on a mass of molten metal, for example aluminum, are much greater than would ordinarily be expected from the chemical reaction of the small amount of flux. Assuming that we can write the equation for all the chemical reactions taking place when the flux is added, the real fluxing action must still be explained. The mere knowledge of existing chemical changes does not account for the physical changes observed.

In fluxing molten metal two phenomena are usually observed; *viz.*, the metal appears to be less viscous and a varying amount of dirt or powder rises to the surface of the metal, which is skimmed off before the metal is poured. The common explanation for the first effect is that impurities have been removed from the metal, as evidenced by the accumulation of powder on its surface.

The true viscosity of molten metals is very low, being about the same as the viscosity of water, which makes the determination of absolute viscosity difficult and renders the determination of small variations in viscosity, due to the effect of dissolved oxides, well nigh impossible unless one goes to the most exacting extremes in apparatus design. The presence of impurities, sometimes suspended in the metal and sometimes dissolved, makes it impossible to use the capillary tube for testing the viscosity of flow, since these impurities soon change the cross-section of the tube and introduce errors of great magnitude. The value is so low that to measure the viscosity by the rotation of a cylinder within a cylinder necessitated the most delicate and frictionless bearings. The influence of the surface film on the rotating cylinder supports is sufficiently great to interfere with all tests. The experiments of the writers to determine viscosity and viscosity changes due to fluxing show that this property is but little changed by the process of fluxing, and that it is the change in the surface film which accounts for the apparent change in viscosity. A further confirmation of this lies in the fact that, in the case of aluminum, the writers have been unable to note any difference in chemical composition or amount of dissolved oxide before and after fluxing.

The dust or powder found on the surface is derived partly from the interaction of the flux with the molten metal, and not the oxide, and partly from the surface film. By surface film is meant not only the surface in contact with the atmosphere but the film that surrounds the molten metal as a whole, most of which is in contact with the walls of the retaining vessel. A large portion of the powder evidently arises from the walls of the crucible, a change in the strength of the surface film allowing

it to become free and float to the surface. In the case of aluminum, no chemical reaction is possible between the fluxing chloride and the oxide of the metal; the effect of the flux is to change the strength of the surface film, probably by breaking it up mechanically by the volatilization of the flux.

Nature and Amount of Impurities

The complete experiments on the nature and amounts of impurities made by the authors are limited to the solid impurities introduced into commercially pure aluminum by melting in an oxidizing atmosphere in different kinds of crucibles, and to the solubility of hydrogen in molten copper and its alloys. The latter experiments form the subject of a separate paper, but are outlined here.

Aluminum was heated, without stirring, for 8 hr. at about 750° C. in different kinds of small crucibles placed in a Hoskins resistance furnace, the door of which was left slightly open. The results obtained are given in Table 1. The soaking action in these experiments was carried far

Table 1.—*Results of Heating Aluminum in Crucibles of Different Kinds*

Crucible	Al_2O_3, Per Cent.	Fe, Per Cent.	Cu, Per Cent.	Silicon, Per Cent.	
				Total	Graphitic
Original ingot	0.35	0.34	0.1	0.3	
Pressed steel	0.4	0.5	0.12	0.3	
Acheson graphite block	0.4	0.29	0.1	0.23	
Dixon graphite-clay	0.9	0.34	0.1	0.25	
Magnesia	1.3	0.36	0.13	0.3	
Clay	2.7	0.40	0.1	0.94	
Porcelain (glazed)	7.5	0.45	0.1	3.0	2.8
Sand	11.4	0.3	0.1	6.4	5.8
Fused silica	14.7	0.3	0.1	11.3	11.0*

* Crucible turned black in contact with metal.

beyond the point reached by even the poorest commercial practice. However, the tendencies of certain kinds of crucibles to introduce impurities is shown, as is the fact that even with prolonged heating in exposure to air aluminum does not take up much oxide from surface contact with the atmosphere. On prolonged heating in refractories containing even combined silica, reduction takes place with the introduction of alumina and it is conceivable that in commercial practice appreciable amounts of these impurities may be introduced. However, in common practice crucibles or refractories containing silica are not used in the melting of aluminum.

The extent to which it is possible to load aluminum with its oxide, under certain conditions, is surprising. In the case of the extreme

amounts, a microscopic examination showed that much of the oxide was suspended and not dissolved and that it was not uniformly distributed. A sample of so-called secondary, or recovered, aluminum, which had probably been made by a rather simple process of remelting aluminum turnings, was found to contain 2.27 per cent. Al_2O_3, 1.21 per cent. Fe, and only 0.25 per cent. Si, indicating that the melting had taken place in iron vessels, unless the refiner had carelessly failed to remove the free iron from the turnings before melting. With the ordinary remelting of finely divided aluminum, such as turnings, it is well nigh impossible to avoid the introduction of alumina. Commercial aluminum containing 0.1 per cent. copper was melted in a crucible with the careful addition of the same weight of fine turnings, care being taken to avoid oxidation as much as possible. After allowing the metal to stand for a short time, it was skimmed and poured. The oxide content was found to be 1.3 per cent. On repeating the experiment, adding the turnings and stirring in a manner calculated to be most detrimental to the metal, the oxide content was 10.5 per cent.

The determinations of alumina were made, according to the method of Rhodin,[2] by dissolving in 10 per cent. NaOH solution and were checked by dulplicate analyses, using 5 per cent. hydroxide solution. The agreement was satisfactory, being within 0.2 per cent. on samples containing 3.2 per cent. oxide. The method was substantiated in the case of several complete analyses in which the aluminum was determined directly; for instance,

	Sample No. 1 Per Cent.	Sample No. 2 Per Cent.	Sample No. 3 Per Cent.
Al_2O_3	0.43	7.2	10.5
Fe	0.29	1.2	1.4
Cu	0.20	9.5	9.5
Si	0.23	0.5	0.3
Al	98.5	81.3	78.7
	99.65	99.7	100.4

(Average of duplicate analyses on each sample.)

Duplicate analyses on samples containing high amounts of oxide were sometimes not good, indicating that the oxide was not uniformly distributed through the metal.

Gases in Molten Copper and Brass

The amount of hydrogen that can be liberated from molten copper and its alloys upon solidifying and cooling to room temperatures has been determined.

Molten copper will absorb considerable hydrogen if exposed to hydrogen or if its surface or the containing graphite crucible is bathed with a

[2] *Loc. cit.*

gas flame; the amount absorbed is dependent on the temperature of the molten metal. A large portion of this dissolved gas will be given off in the process of solidifying and cooling. The amounts evolved at different temperatures of saturation are, approximately, as given in Table 2.

TABLE 2.—*Hydrogen Evolved from Copper at Different Temperatures*

Temperature of Saturation, Degrees C.	Hydrogen Evolved	
	Milligrams per 100 gm. Metal	Volume* per One Volume of Metal
1100	0.600	3.33
1150	0.725	3.42
1200	0.85	4.00

* Volume is at 760 mm. and temperature of solidification is 1083° C.

Similar conclusions apply to copper alloys containing zinc or tin, or both, the amounts being as follows:

Copper in Brass, Per Cent.	Temperature of Saturation, Degrees C.	Hydrogen Evolved	
		Milligrams per 100 gm. Metal	Volume per one Volume Metal
95	1140	0.62	3.0
90	1100	0.52	2.2
85	1100	0.47	1.8
80	1100	0.41	1.6
75	1040	0.34	1.2
70	1000	0.17	0.75
65	985	0.25	1.0
60	975	0.33	1.2
55	950	0.16	0.5
50	930	0.08	0.2
45	920	0.05	0.1
40	920	0.02	0.05
35	910	0.01	0.03
95 Tin 5 per cent.	1150	0.70	
90 Tin 10 per cent.	1150	0.60	
Red brass	1150	0.53	
Admiralty bronze	1150	0.56	
Yellow brass	1150	0.36	

Hydrogen will penetrate into the metal through many of the usual coverings but it is retarded by boric oxide and by a mixture of lime and soda ash. It is not retarded by a mixture of lime and fluorspar as is frequently stated. Dissolved hydrogen is removed as water vapor, to a large extent, by the addition of excess amounts of zinc oxide, or cuprous oxide dissolved in copper. Ordinary fluxes apparently do not have much, if any, effect upon it, nor do the metal scavengers called deoxidizers.

Chemical Action of Fluxes

Whatever chemical reactions we may anticipate in the use of fluxes may be considered in connection with the different classes of fluxes: chlorides, oxide slags, and deoxidizers.

Chlorides

The common chloride fluxes used are zinc chloride, ammonium chloride, and sodium chloride. With these chlorides two possible chemical reactions may be expected—that between the chloride and the oxide of the metal and that between the chloride and the metal itself. These would be illustrated, in general, by the equations:

With oxides $MO + ZnCl_2 = MCl_2 + ZnO$

$MO + 2NH_4Cl = MCl_2 + 2NH_3 + H_2O$

$MO + 2NaCl = MCl_2 + Na_2O$

With metals $M + ZnCl_2 = MCl_2 + Zn$

Zn may then alloy with excess of the metal.

$M + 2NH_4Cl = MCl_2 + 2NH_3 + H_2$

$M + 2NaCl = MCl_2 + 2Na$

Sodium volatilizing or alloying with the metal.

An explanation of the action of these chlorides in fluxing is commonly given in the literature in accord with the first group of equations. The chloride fluxes, by reaction with the oxide impurities in the metal, convert these to chlorides which are either volatilized out of the metal or float to the surface. Anyone who has experienced the somewhat slow alloying of metals of nearly the same gravity would find it difficult to believe that in the incredibly short time of action of these fluxes, small quantities of these volatile materials can be added to the surface of a molten metal and by stirring be made to diffuse through the mass of the metal so that the disseminated oxide molecules are sought out and brought into chemical reaction. Such chemical reactions between the oxides and chloride fluxes are in many cases quite possible and may occur to some extent in fluxing. It must be quite apparent that this is not the main action involved since, in the case of aluminum, there is no action between aluminum and these chlorides at the temperatures involved in fluxing, yet ammonium chloride and zinc chloride are commonly used in aluminum casting and produce marked and almost instantaneous effects on the molten metal.

This rapidity of action and the resulting physical effect, which is apparently all out of proportion to the amount of flux added, are shown best when zinc chloride is added to a sluggish bath of aluminum which is somewhat impure or to a hot mass of finely divided aluminum chips or grindings that have been heated above the melting point of the metal but which refuse to coalesce. The addition of a relatively small amount of zinc chloride gives the effect of suddenly acquired fluidity to the bath,

while the small particles in the second case unite rapidly to form a quantity of molten metal. The second case probably shows the way to the real explanation of fluxing, since in this instance we are dealing with a surface phenomenon and the flux does not have an effect on the interior of these small particles. The time element points away from a purely chemical explanation of fluxing.

The second group of equations, while possible in many cases, would not suffice as an explanation involving the removal of impurities in the metal. For the sake of completeness, however, it may be well to test these reactions to know which can take place at the temperatures commonly used. This may be done in a qualitative way quite readily and if an action takes place the temperature at which it becomes apparent may be recorded.

A summary of a group of experiments made by heating the reacting substances in suitable tubes and sweeping away volatile products by an inert gas (nitrogen) is given in Tables 3 and 4.

TABLE 3.—*Oxides with Fluxes*

Oxide	$ZnCl_2$, Degrees C.	NH_4Cl, Degrees C.	NaCl, Degrees C.
ZnO	400	400	No action
PbO	350	350	No action
SnO_2	350	300	No action
Al_2O_3	No action	No action	No action
Cu_2O	550	350	780–800 (chlorine evolution[a])
CuO	550	350	900 (chlorine evolution[a])
Fe_2O_3	No action	500	No action
Cr_2O_3	No action	500	No action
Maximum temperature of experiment	1000	1000	1000

TABLE 4.—*Metals with Fluxes*

Metal	$ZnCl_2$, Degrees C.	NH_4Cl, Degrees C.	NaCl, Degrees C.
Zinc	No action	400	No action
Lead	350	350	No action
Tin	300	300	No action
Aluminum	400	400	No action (?)
Copper	300	350	850
Iron	500	400	1000
Chromium	1000	450	1000
Maximum temperature of experiment	1000	1000	1000

[a] Cuprous oxide reacts with sodium chloride at 750° to 800° with formation of cuprous chloride and evolution of chlorine. Chlorine is also evolved when cupric oxide is heated to 900° with sodium chloride due to the decomposition of the cupric chloride formed by the original reaction.

Fluid Covers

The object of coverings is supposedly to protect the metal from gases, although some coverings have been added with the intent to duplicate the metallurgical fluxes or slags by uniting with the metallic oxides present. Thus in melting fine particles of aluminum, cryolite mixtures are used with the intent of dissolving the oxide layer on the particles. Such uses are, however, not a regular foundry practice and belong in the field of metallurgical fluxes.

It sometimes happens that a covering for molten metal will dissolve the metallic oxides present to some extent. Coverings containing borax or boric oxide are especially active in this manner. The action is limited by the amount of stirring or circulation of the metal, since the reaction takes place only at the surface. It is conceivable that the metal near the surface would have its oxide content lowered by solution in the covering, which would cause a diffusion of the oxide from the interior portions richer in oxide, until in time we might have quite an appreciable amount of oxide dissolved in the covering.

A sample of impure commercial No. 8 aluminum alloy was melted under boric oxide for 30 min. with frequent stirring with the apparent change indicated by the following analyses:

	Al_2O_3	Fe	Si	Cu
Original metal	2.27	1.21	0.25	7.7
After melting	1.7	1.4	0.28	7.7

The oxide was determined after the method of Rhodin[3] by solution in 10 per cent. sodium hydroxide solution.

The object of protecting the metal by molten coverings is frequently not attained since many of the common coverings are penetrable readily by hydrogen, and in crucible furnaces hydrogen will pass rapidly through the walls of the hot crucible.

Deoxidizers

The chemistry of the deoxidizers is well known. As a class they are either metals or compounds capable of uniting with oxygen with evolution of a great amount of heat and thus able to take oxygen away from the metals which have a lower heat of oxide formation. Their oxides are either volatile, as phosphorus oxide, or rise to the surface of the molten metal from which they may be skimmed. The amounts required depend on the amount of oxide impurities in the metal to be treated. Studies on the amounts of deoxidizers required or of the relative efficiencies of the different deoxidizers must be undertaken with proper control of the melting conditions, and it should be borne in mind that conclusions reached under one set of conditions do not necessarily apply under other conditions. In the following experiments, the effort was made to maintain conditions constant.

[3] *Loc. cit.*

Various commercial deoxidizers were added to the highest grade lake copper. The copper was raised to the pouring temperature 1150° C., the deoxidizers added, the metal rapidly stirred, and the metal held without stirring at the pouring temperature for 20 min. before pouring into sand molds. The melting was done in an electric furnace of the carbon-resistor type, so designed as to reduce the absorption of gases to a minimum. The metal was poured into sand molds to give bars for conductivity tests (½ by 18 in.). Samples of the bars were taken for microscopic examination.

The percentages of deoxidizer shown in Table 5 are those of active material added on the basis of chemical analysis of commercial deoxidizers, which were approximately 15 per cent. phosphor-copper, 10 per cent. copper-silicon, 24 per cent. manganese copper, 99 per cent. aluminum, 100 per cent. zinc, 100 per cent. magnesium. No analysis of boron carbide being available, the additions were made on the basis of 100 per cent. active material.

TABLE 5.—*Deoxidizers with Copper*

Deoxidisers,	Per Cent. Cu_2O	Soundness of Copper Castings	Excess of Deoxidizer, Per Cent.	Electrical Conductivity
0.005 Per Cent.				
Si	0.3	Poor	0.0	
P	0.8	Fair	0.0	
Mn	0.8	Good	0.0	
Al	2.0	Fair	0.0	
Zn	2.0	Poor	0.0	
Mg	1.7	Fair	0.0	
B_6C	0.1	Poor	0.0	
0.05 Per Cent.				
Si	0.0	Poor	0.0	
P	0.0	Good	0.0	83.4
Mn	2.0	Fair	Small amounts	
Al	0.0	Fair	Some	
Zn	0.5	Fair	0.0	
Mg	2.0	Fair	0.0	
B_6C	0.0	Good	0.0	95.7
Ce	3.0	Poor	0.0	
0.5 Per Cent.				Dissolved Deoxidizer (Coring)
Si	0.0	Good	0.0	Slight
P	0.0	Fair	Some	Much
Mn	0.0	Fair	Some	
Al	0.0	Good	0.0	Some
Zn	Considerable	Poor	0.0	Slight
Mg	0.0	Fair	0.0	Very slight
B_6C	0.0	Fair	0.0	

Oxide formed by action of the deoxidizer and remaining in the metal was found with aluminum, zinc, and magnesium.

The results obtained are not satisfactory since few of the castings made could be machined into a fine rod for conductivity measurements, weakness, and internal blowholes developing upon machining. Since every effort was made to prevent absorption of gases, it is probable that the difficulty came from the molding sand or the method of casting. The authors, therefore, would not attempt to make any comparisons as to the efficiency of the various deoxidizers from a commercial standpoint without a very careful repetition of these experiments. Under the conditions of use, which apparently were not the best, copper, phosphorus, and boron carbide appeared to be superior to the other deoxidizers.

The results may be of interest as indicating the conditions of equilibrium. Thus, 0.005 per cent. of active deoxidizer was insufficient in all cases for the complete removal of the copper oxide. Copper oxide was completely removed by the silicon, phosphorus, aluminum, and boron carbide added in amounts of 0.05 per cent. of the weight of the co per and there was no excess of deoxidizer apparent in the case of the silicon, phosphorus, and boron carbide. Manganese did not remove the oxide, although added in excess, while this percentage of zinc or cerium was not sufficient to remove the oxide; 0.5 per cent. of deoxidizer appeared to be more than was required for the removal of copper oxide, with the exception of zinc.

Deoxidation with Ammonia

Some experiments were run by bubbling dry ammonia gas through molten copper. It was found that the ammonia removed the copper oxide in 15 min. or less but in so doing saturated the metal with hydrogen. With the particular molds and sand used, it was nearly impossible to control the rate of cooling and to provide for the removal of the dissolved gas. As a result the test pieces were very porous. One piece was obtained which machined nicely and was quite sound. The electrical conductivity (volume) was 93.98 per cent.

Deoxidation by Alloying Metals

The addition of many of the common alloying metals to copper accomplishes the removal of copper oxide. The alloys thus formed are usually characterized by a selective oxidation in the molten state, the oxide of the alloying element forming instead of copper oxide. The study of the equilibria between various pairs of common elements and oxides at temperatures corresponding to the pouring ranges of the commercial alloys affords an interesting field for research; the authors have prepared samples that are awaiting analysis.

Zinc was found to reduce Cu_2O at 450° C.; tin, between 600° and 800° C.; while lead was without reaction at temperatures below 360°. These reductions should be borne in mind in considering the nature of oxide

impurities which form by oxidation of the molten metal, thus as long as brass contained free zinc we should expect to find copper oxide as an impurity.

Physical Action of Fluxes

As stated before, the physical action of fluxes is very rapid and appears to be greatly out of proportion to the amount of flux added. In discussing the effects of fluxes, it is necessary to consider each class separately. We have no evidence that the chloride fluxes produce any change in the composition of the metal, the chloride coverings may remove metallic oxides to some extent, while the deoxidizers accomplish this result much more effectively. The physical effects of the chloride fluxes will then be largely those produced by surface changes, but these changes may be great and of considerable practical importance. The changes produced in the metal in the second class are incidental and need not be considered here. In the case of deoxidizers there is more or less complete removal of oxide impurities. If these oxides are merely suspended or physically mixed with the metal, the physical changes in the metal will not be great except where a surface change is produced at the same time. If, however, the deoxidizer removes an oxide from solution in the metal such physical properties of the metal as melting point, viscosity, and surface tension may be changed. These changes on the molten metal are likely to be small in comparison with surface changes. Their effects on the physical properties of the cast metal, on the other hand, may be great, as in the case of copper in which they change nearly all of the mechanical properties and the electrical conductivity.

The surface of many molten metals becomes covered with a surface film of mixed oxide and metal. While the thickness of the film appears to be greatest where it is in direct exposure to the air, it seems to surround the molten metal more or less completely. The effect on the mobility of the molten metal is to give an effect of increased viscosity. It is similar to surrounding a mass of water by a thin rubber wall. The mobility of the mass would be changed greatly while the rubber wall would be without effect on the viscosity of the water. The tenacity of the surface film is very great in the case of aluminum. With copper, the film does not form to a similar extent on account of the solubility of the copper oxide in molten copper. There must, of course, be some affinity between the oxide and the metal, at least sufficient to cause wetting, or the film would not be tenacious. In handling the metal, the increased viscosity due to the film has undesirable effects, such as interfering with proper stirring and preventing the metal from flowing freely into and filling in sharp corners of a mold.

The effect of the film is noticed in attempting to melt finely divided metal, such as aluminum. The metal may be heated considerably above

its melting point without the particles coalescing. They may become almost spherical and consist of molten metal surrounded in a bag of surface film. The globules may touch each other but the films prevent the metal from collecting in larger particles. If the films are broken mechanically, the particles will unite. The effect of fluxes upon these films has already been discussed under the head of chemical action. In the case of aluminum, the chloride fluxes cannot react chemically with the film itself; they may react with the metal underneath if they are able to penetrate through the surface film.

We are, therefore, forced to the conclusion that the real action of such fluxes is physical in nature. It may be largely mechanical. That is, the rapid evaporation of the flux at the points of contact with the surface film may mechanically break the film, allowing the molten particles to unite. The flux may penetrate through the film and react with the metal below, giving a volatile substance which disrupts the film. Since the fluxes themselves and the volatile products, possibly by a chemical reaction, are of about the same volatility, this explanation does not appear to hold. In certain experiments, the writers have conducted vapors of these fluxes over oxide films on finely divided particles of aluminum without causing the union of the particles. On the other hand, it has been possible by suitably protecting the finely divided metal particles from oxidation to cause a complete coalescence by mechanical means without addition of a flux. This mechanical explanation was long ago advanced by Gillett, after considerable experience in the melting of aluminum filings and turnings. The authors have been able to cause good fluxing of finely divided aluminum particles by adding aluminum chloride, which is the reaction product of any possible chemical reaction with the original chlorides and which is itself without chemical action on the metal or the oxide. The action would seem to be mechanical without a doubt.

Another possible explanation would be the partial solution of the surface film in the thin layer of molten flux that exists before the flux is volatilized, which causes a weakness in the film and allows it to break. We have no experimental evidence of this.

DISCUSSION

T. P. Thomas.—When a metal chloride flux is added to a charge of molten metal, two possible chemical reactions may result—that between the chloride and the metal and that between the chloride and the oxide of the metal. In the former reaction the metal resulting from the reduction of the flux may either volatilize or alloy with the metal to be fluxed, while in the latter reaction the metal unites with the oxide impurities in the charge and floats to the surface.

H. J. ROAST,* Montreal, Que.—When brass is poured through a molten borax flux, the borax does not go into the casting. In England, in making alloys of gold and silver, borax was used as a cover; also when casting brass when we did not wish to have anything wrong with the cross-section of the bar, which is often polished. There is no difficulty at all in getting the metal free from occluded borax flux. Fluxes are used to keep away the air and the flux that will melt at a temperature nearest to the temperature of the molten alloy is the best for the purpose.

F. A. SCHUTZ, Decatur, Ill.—Borax injures the crucibles to such an extent that they will give only one-half as many heats as they would otherwise. My experience is that charcoal and glass make the best flux. It is dirty but it does not affect the crucible and the metal comes out in the best condition. Any kind of glass may be used. At one time the use of colored glass was advocated but nothing is gained by its use. In a Schwartz furnace I use borax. Much of the trouble is due to a desire to get out the greatest possible number of heats in a day. As a result the temperature is raised so rapidly that the outside of the metal is burned before the inside is melted.

W. V. BERRY, New Brighton, Pa.—The glass forms a slag that protects the metal from the occluding gases while the charcoal has a tendency to take the oxygen or hydrogen from the metal.

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Roasting and Chloridizing of Bolivian Silver-tin Ores

By M. G. F. Söhnlein, E. M., Santiago, Chile, S. A.

(New York Meeting, February, 1921)

In the metallurgical treatment of sulfide silver-tin ores mined at Oruro, Potosí, and Chocaya, the most important and difficult step is chloridizing-roasting. The ores are chiefly mined from veins in rhyolite, a detailed description of which can be found in most textbooks on ore deposits. The chief gangue minerals are pyrite and quartz, and the silver content is derived from tetrahedrite, jamesonite, stibnite, and cylindrite. Most of the tin is present in the form of a rather impure cassiterite, which forms microcrystalline aggregates of varying richness with quartz and pyrite; occasionally, some tin is found as stannite, cylindrite, and other complex sulfantimonates. The silver content of the minerals that compose the ore is approximately as follows: Pyrite, 3 to 5 oz. per ton; jamesonite, 30 to 50 oz. per ton; galena, 40 to 50 oz. per ton; stibnite, 30 to 150 oz. per ton; cylindrite, 200 to 300 oz. per ton; tetrahedrite, 500 to 3000 oz. per ton. Occasionally, some ruby silver ore is found, but it is very rare. In the mines of Oruro, which are the deepest in the sulfide zone, tetrahedrite has nearly disappeared, stibnite, jamesonite, and, in the deepest levels, cylindrite taking its place.

At present, there are six mills treating this ore, two at Potosí, two at Chocaya, one at Poopo, and one at Machacamarca. The ore is crushed dry, given a chloridizing roast, leached with water and hyposulfite solution (or with brine) to extract gold, silver and copper, and concentrated for tin with or without regrinding.

Early Ore-treatment Methods

In the earlier days, these ores were treated by chloridizing-roasting followed by amalgamation, with satisfactory results, according to the information now available. Material from old tailing dumps from ore treated by this process, which are found at several places in the vicinity of Oruro, seldom contains more than 5 to 6 oz. of silver per ton. As ore with less than 100 oz. per ton was not treated, the extraction of silver must have been good. Reports of the operating companies published about 1890 asserted that over 90 per cent. of the silver was recovered, but in these calculations, as a rule, no allowance was made for silver lost during roasting and the figure referred only to the extraction of silver by amalgamation from the roasted ore.

Between 1890 and 1900, amalgamation was replaced by leaching with either hyposulfite solution or brine. It is remarkable that tailings from high-grade ore treated by amalgamation and those derived from ores of much lower grade that have been leached contain about the same amount of silver, namely, from 5 to 7 oz. per ton. The percentage of chloridizing that can be obtained is not directly proportional to the silver content of the ore, but it seems as if the quantity of silver that cannot be converted into chloride is more or less constant. For instance, after roasting an ore containing 25 oz. per ton, the amount of silver that cannot be chloridized will be 5 to 6 oz. per ton; whereas, with ore of 100 oz. per ton, after roasting, there will be from 8 to 9 oz. of insoluble silver. The silver that has not been chloridized and is left in the tailing after amalgamation or leaching cannot be dissolved by cyanide or any other commercial solvent known to the writer. Only a small proportion of it is contained in sulfides that have remained undecomposed owing to imperfect roasting; if these tailings, after fine grinding, are treated by flotation, a small amount of concentrate having about the same silver content as the original ore can be obtained but the amount extracted is insufficient to pay for this treatment.

On account of the difficulty, expense, and silver loss connected with chloridizing-roasting, more direct treatments have been tried for these ores. Agitating the raw ore with cyanide or bromine cyanide after fine grinding is absolutely ineffective; neither can commercial results be obtained by attempting to decompose the sulfantimonates with metallic aluminum, followed by cyanide treatment. This experimenting was carried out chiefly by one of the best known ore-testing laboratories in the United States. Cyanide consumption on either raw or roasted ore was excessive, and the extraction obtained by agitating the finely ground roasted and chloridized ore with cyanide was not better than by leaching the same material at 16-mesh with hyposulfite. Therefore, thus far the old method has proved to be the only way of treating these ores; and to increase the mill capacity and decrease the cost, it was necessary to find a mechanical furnace that would perform roasting and chloridizing as well, or better, than the old hand-rabbled reverberatory furnaces.

All these ores contain from 25 to 35 per cent. sulfur. In some plants, it is customary to give the ore, before crushing, a preliminary roast in kilns, which reduces the sulfur content to 8 to 10 per cent.; this has the advantage of making the ore more easy to crush. The partly oxidized ore, after having been ground to about 1 mm. is fed to hand-rabbled reverberatory furnaces where the remainder of the sulfur is driven off and salt is added to complete the process. This second roast has to be carried out with the addition of fuel, because most of the sulfur has been lost by kiln treatment; and since fuel is expensive in Bolivia, it is cheaper to omit kiln roasting, crushing the raw ore at once to the fineness required

(which varies between 2 mm. and 0.6 mm.) and roasting and chloridizing without fuel or with a much smaller amount. In former days, when good crushing machinery was unknown here and the cost of power was nearly prohibitive, kiln roasting was justified, but under present conditions it is not. Besides, it requires more handling than direct crushing and roasting. I have not been able to ascertain whether silver is lost during kiln roasting. A few tests were made with a kiln holding about 750 kg. of ore, which varied in size from 2½ to ½ in. (6.4 to 1.3 cm.), and one quarter of the charge was taken as a sample. One test showed an appreciable loss in silver, but in two others there was a gain in silver, which is impossible, so that the material was too coarse to give a reliable sample.

Early Chloridizing Methods

Chloridizing is simple and quick if salt is added at the correct stage of the roast. If salt is mixed with the ore before nearly all the sulfur has been converted into sulfates, it will retard roasting and increase volatilization losses; besides, salt is consumed unnecessarily. If the salt is added too late, it will fail to react properly and too low a percentage of silver will be converted into chloride. In hand-rabbled furnaces, the correct amount of salt is 3.5 per cent. for an ore of 25 oz. per ton and 5 per cent. for 50-oz. ore. An excess of salt has no particularly harmful effect on the process, but the excess is left undecomposed in the roasted ore, and during the water-wash that precedes hyposulfite leaching, it forms brine which dissolves silver chloride.

Usually the hand-rabbled reverberatory furnace has one continuous hearth, 10 ft. (3 m.) wide, divided into three sections 10 ft. long. There is a drop of 4 in. from one section to the other, the highest being next to the flue, where the raw ore is charged through a drop hole in the arch. A charge of 700 kg. is brought into the furnace and rabbled until it ignites. During normal operation there is a charge in each section of the hearth and care is taken that no ore is rabbled into the section lower down than it belongs. If the charge on the third section is so far roasted that it shows but a few sparks when rabbling, the salt is shoveled into the furnace. The decrepitation of the salt causes violent dusting; therefore, the draft of the furnace is shut off until decrepitation ceases. After the damper is again opened, the charge is rabbled until chloridizing is completed, when the ore will not flow but packs together somewhat like snow and stands up with nearly vertical sides. The chloridizing takes a little less than 1 hr. in these furnaces; once the ore begins to pack, it is useless to continue rabbling, because the percentage of chloridizing is not increased. If worked by two men, one furnace has a capacity of 4 to 4.5 metric tons per 24 hr. A little taquia fuel (llama dung) is used during chloridizing, because it is not possible to rabble the charge during

chloridizing as continuously as during oxidizing, on account of the corrosive fumes that escape through the working doors, for, to keep down the volatilization losses the furnace is worked with a reduced draft.

A charge remains about 4 hr. in each section and is in the furnace altogether 12 hr., of which less than 1 hr. is used for chloridizing. It would therefore be a mistake to try to chloridize continuously, adding salt to the last hearth or section of some kind of mechanical furnace, because the atmosphere in the furnace would be charged with chlorine which retards roasting and attacks the metal parts. Moreover, continuous work has the disadvantage that, if ore with insufficient or too much sulfur enters the chloridizing section poor work will be done until conditions are improved, which will take considerable time with a roasting furnace of some size.

Satisfactory metallurgical results are obtained from hand-rabbled furnaces worked by competent men; formerly, these could be found as chloridizing roasting has been practiced in Bolivia for generations. The average silver loss caused by dusting and volatilization during a period of several years was calculated to be 6 to 7 per cent. at Machacamarca; if the furnace is worked carefully, the loss can be reduced to a lower figure as was proved by an experiment described later. The cost of roasting was not high, being around $2 (U. S. currency) per metric ton, including everything, but as the plants grew in size and tin mining drew a large percentage of the men away from the silver mines, it became imperative to use mechanical furnaces.

Roasting Huanchaca Ore

The Compañía Huanchaca de Bolivia led the way in installing a mechanical roasting plant. The Huanchaca ore is a heavy sulfide with a large proportion of blende; it carries no tin but contains similar silver minerals and is treated by the same process as the ores referred to in this paper; therefore, a short description of the plant is of interest. The ore was given an oxidizing roast in Kaufmann furnaces, which are small circular, superimposed hearth furnaces of the McDougall type, and the product from several of these was fed to a furnace of the same type where it was mixed with salt and chloridized. This installation was not satisfactory, the loss of silver through dusting and volatilization was much higher than in the hand-rabbled reverberatories and chloridizing was not as good. The latter was due to changes in conditions in the oxidizing furnaces; the slightest change in fineness or sulfur content of the ore, or of the temperature of the furnaces would result in a product with either too much or not sufficient sulfur being delivered to the chloridizer. Further, because of continuous contact of the furnace shaft and rabbles with chlorine fumes, these parts corroded quickly and had to be replaced

every four or five months. The furnaces were only air cooled; if water cooling had been used the material might have given longer service. For these reasons, the chloridizing furnace was abandoned and the product from the oxidizing roasters was fed to ordinary hand-rabbled reverberatories and chloridized in the old way. Although this arrangement dispenses with considerable labor, it requires strong and skilled workmen. It also has the same disadvantage as the mechanical system; that, if conditions in the first stage of roasting are not kept strictly uniform, and it has been proved that this is not possible, chloridizing will be unsatisfactory. I am indebted for this information to Mr. L. Wurhaft, formerly metallurgist to the Huanchaca Co.

First Mechanical Furnace at Machacamarca

The first mechanical furnace installed at the Machacamarca plant of the Compañía Minera de Oruro was a six-hearth McDougall with an inside diameter of 14½ ft. (4.4 m.). It was first used in connection with two hand-rabbled chloridizing furnaces, where the calcines were mixed with salt. The furnace was fed with ordinary run-of-mine ore which contained about 35 oz. of silver per ton and 30 per cent. sulfur; the product from the McDougall contained from 4 to 4.5 per cent. sulfur. It was soon evident that the silver losses in the McDougall furnace were much higher than in the reverberatory furnaces. The loss of weight during roasting is from 18 to 20 per cent. on an ore with about 30 per cent. sulfur; therefore, if the raw ore assays 35 oz. per ton, the roasted ore should contain approximately 42 oz. per ton if no silver were lost during roasting. Instead of this, the product from the McDougall furnace assayed, usually, a little less silver than the raw ore, which proved that at least 20 per cent. of the silver passed through the stack. Later tests proved this loss to be much higher. The capacity of the furnace was 20 metric tons per 24 hr. when roasting from 30 per cent. sulfur to about 4 per cent. Water cooling was used, because on a 30 per cent. sulfur charge, the furnace would run so hot that if no particular care was taken, the ore would sinter on the third hearth, causing frequent breakage of rabble teeth. The higher the temperature, the heavier were the silver losses through volatilization. The economy in labor was not as great as had been expected, because one attendant was needed for the McDougall and four furnacemen were required at the reverberatories for chloridizing. These men could have roasted and chloridized 9 tons per day, using the reverberatories without the McDougall, so that the cost of labor was only reduced to about 45 per cent.

It was therefore evident that the furnace should be used in some other way. For some time, the attempt was made to assist chloridizing by feeding salt continuously into the furnace on the fifth hearth. The rabbles are so set that on this hearth the ore is moved from the periphery to

the center, so that, if salt was fed through one of the working doors on the fifth hearth chloridizing was carried on on the entire surface of the fifth and sixth hearths. But at this point the ore was not sufficiently roasted to react well with the salt, and the final product from the furnace contained too much sulfur and unchloridized silver to allow dispensing with finishing in the reverberatories. Later, in order to reduce the heavy losses of silver, the furnace was used only for roasting ore containing from 12 to 15 oz. of silver per ton with about 25 per cent. sulfur, but even on this material the silver losses were entirely too high.

The charge for the McDougall furnace is now prepared by mixing low-grade fines of run-of-mine ore with high sulfur content with silver-tin ore which carries only 15 to 20 per cent. sulfur. When working on this ore the furnace has a maximum capacity of 22 metric tons per 24 hr. and delivers its product to one reverberatory furnace for finishing and chloridizing, instead of to two furnaces as was the former practice. On ore with more than 30 per cent. sulfur, the capacity is only 17 tons. No fuel is used in the McDougall, but a small amount must be supplied to the reverberatory furnace so as to keep its temperature high enough for continuous chloridizing. The difficulty common to all continuous chloridizing is experienced here—slight variations in the McDougall furnace caused by different composition of the ore, etc., is at once reflected in the results. An attempt to remedy this was made by placing a small bin between the McDougall and the reverberatory, where the partly roasted ore could be stored, if it came down with too much sulfur. With this arrangement, two men working at the reverberatory furnace could finish roasting to the desired point without having to add the salt, and if the ore came down with too much sulfur, the charge to the furnace could be at once reduced. But it takes several hours to bring the McDougall furnace back to proper conditions, and if too much half-roasted ore was held in the bin, it became too cold for chloridizing, so that this arrangement was not satisfactory. Often some of the ore had to be chloridized before it was properly roasted to prevent its becoming so cold that it would spoil the work of the reverberatory roaster altogether. If, on the other hand, the ore came down too far oxidized, chloridizing would be bad because the salt could not react properly with the ore; there was no remedy for this, except mixing with elemental sulfur before chloridizing, which procedure is far too complicated and too expensive for practical work.

Losses Through Dusting and Volatilization

Losses of silver through dusting and volatilizing can be prevented by passing the roaster gases through a Cottrell precipitator. Experiments made by a representative of the International Precipitation Co. showed that 9500 cu. ft. of gas containing 0.32 gm. of solids passed each minute out of the stack of the McDougall furnace. Therefore, 4300 kg. of dust

were carried away per 24 hr. At that time the feed to the furnace was 22,400 kg. per 24 hr. of ore carrying 670 gm. silver per ton. The sample collected in the filter assayed 1070 gm. per ton; therefore, a little over 30 per cent. of all the silver that goes to the furnace is lost through the stack. The flue dust is a mixture of totally oxidized, half oxidized, and raw ore, and contains considerable antimony trioxide. The erection of a Cottrell treater alone would not have solved the problem, for the chief difficulty was the disposal of the dust. (1) It might be returned to the furnace feed; (2) it might be fed, together with raw ore, to one or more of the hand-rabbled reverberatory furnaces; (3) it might be treated separately, without further roasting, by some hydrometallurgical process.

The first method has the advantage of simplicity, but as the gases leave the McDougall furnace at about 180° C., all antimony trioxide driven off would be collected by the Cottrell treater and, since it cannot remain in the furnace on account of the high temperature it would accumulate between the outlet of the McDougall and the Cottrell apparatus, making it necessary to clean the conduits quite frequently, thus causing great irregularity in operating the furnace. It was suggested that the gases be kept so hot that antimony trioxide would not be condensed during their passage through the treater, but this would have been very delicate, and the furnace construction did not allow the construction of the Cottrell treater directly on top of it.

The second way, feeding the dust to other furnaces, has the disadvantage that a certain proportion of the dust would again be lost; and although this scheme on the whole would be feasible, and has been frequently practised here with dust caught in the dust chamber of the McDougall, it is not practical because it reduces the capacity in the other furnaces.

As the dust is a mixture of raw and roasted ore, it seemed practically impossible to obtain a satisfactory extraction by agitation with brine, cyanide, or hyposulfite solutions. Cyanide and hyposulfite failed to extract appreciable amounts of silver, but nearly 60 per cent. could be dissolved by a prolonged agitation of the dust with hot brine, to which a small amount of copper sulfate had been added. The residue of this agitation-leaching was treated by oil flotation, yielding a product of 41 oz. per ton; this brought the total extraction up to 85 per cent. Afterwards an attempt was made to combine the two processes in one operation by agitating with brine and copper sulfate in the flotation machine and adding oil at the same time, but no mineral froth could be formed.

The proposed hydrometallurgical treatment would therefore have consisted of the following processes: Agitation with brine and copper sulfate, precipitating the solution on copper and iron; decantation of the solvent and washing once or twice with water; oil flotation of the residue, filtering and drying the concentrate and feeding it to the reverberatory furnaces

together with raw ore. The same objection, that a certain amount of this flotation concentrate might be carried away again by the draft in the reverberatory furnaces, could be made here, but the sulfide in the dust is much coarser than the oxidized material, since it comes from the upper hearths of the McDougall furnace, where the draft is strongest, and only the finest of the oxidized grains, which come from lower hearths, will finally reach the stack, the coarser ones being again deposited on hearths higher up in the furnace.

The operation of a plant like that described on a basis of about 4 tons per day would be expensive and inconvenient; besides, this treatment is so complicated that perhaps feeding all the dust back to the reverberatory furnaces would have been preferable. Very likely a Cottrell treater would have been installed and the precipitate from it have been treated in the hand-rabbled furnaces, if there had not been developed, just at that time, a system of roasting which made the Cottrell precipitator superfluous.

There is little information available concerning the treatment of dust collected from roaster gases by the Cottrell process. Where ore or concentrate are roasted prior to smelting, the dust is usually bypassed the roasting furnace and sent to the smelter together with the roasted ore. However, I do not know of an instance where roasting is conducted as a preparation for some hydrometallurgical process, and where the dust collected by the Cottrell treater is either treated by a special process or refed to the roaster. Generally, descriptions of plants of this type state that the dust is collected for future treatment. This is unsatisfactory and it is far better to use a type of roasting furnace that does not blow a large percentage of its charge into the air, as do all circular superimposed hearth furnaces, thus requiring the installation of costly and delicate precipitation apparatus which finally recovers the ore that is carried away in the fumes in such a form that the valuable metals from it cannot be recovered.

Straight-line Reverberatory Furnace

The only type of furnace from which any result could be expected was the straight-line reverberatory Edwards or Merton. Furnaces of the revolving drum type, which were formerly extensively used for chloridizing roasting, make as much dust as the superimposed-hearth furnaces of the McDougall type, if not more. Blast roasting could not be used on account of the high sulfur content, and even after having reduced the sulfur by kiln-roasting, there was enough of it left to prevent sintering in the blast-roasting furnace. Moreover, chloridizing was not satisfactory with this treatment.

The next step in experimenting with mechanical roasters at Machacamarca was the erection of a straight-line, one-hearth Merton furnace

with five spindles as shown in Fig. 1. This type of furnace was selected because it fitted best in the plant, the hand-rabbled reverberatories having about the same dimensions. In order to get a good idea of the movement of the ore through the furnace, the ironwork was completely erected before the arch was built. Every spindle had but one rabble arm, which was 5 ft. long, and the rabble teeth were so placed on the arm that one-half of them project forwards about 6 in. and the other half are 6 in. backwards. These teeth are alternated, the object being to have the back teeth cut furrows in the ridges made by the front teeth.

If sand was fed at the center of the first rabble, it was gradually pushed outwards until the last teeth of the second rabble started raking it into the second zone of the furnace, which was formed by the second and third rabbles. The second rabble raked the sand inwards and the third rabble

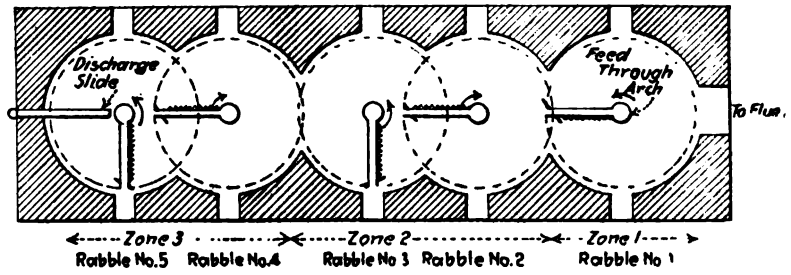


FIG. 1.—STRAIGHT-LINE ONE-HEARTH MERTON FURNACE.

raked it outwards again; no material entered the third zone, which is formed by the fourth and fifth rabbles, until it had traveled nearly the whole surface of the second zone. It was remarkable how well the Merton principle of zone-rabbling worked, and the speed of the driving machinery was so regulated that the material traveled in 8 hr. from the feed to the discharge end. This was supposed to be long enough for good roasting and chloridizing. All rabbles were provided with water cooling. No attempt was made to chloridize continuously as it was thought that better results could be obtained by intermittent work. The five spindles were driven through bevel gears from one shaft, which was cut between the third and fourth spindle, a jaw clutch being placed at this point. This arrangement allowed the independent operation of the fourth and fifth spindles, while the first three were stopped.

The furnace was charged near the center of the first spindle through a drop hole in the arch and the roasted ore was discharged through a radial slot under the last rabble. This slot could be opened and closed by a sheet-iron slide operated from the outside of the furnace.

The operation of the furnace was as follows: After heating the furnace by burning taquia fuel and oil on the hearth at the last four rabbles, ore was fed at the first rabble; after some time the ore would be spread all

through the furnace. As soon as it appeared to be sufficiently roasted at the last two rabbles, the clutch was thrown out (releasing the first three rabbles) and the necessary amount of salt was shoveled in through the working doors at the fourth and fifth rabbles. After chloridizing for about 20 to 30 min., the discharge slide was opened and the chloridized charge drawn off. After closing the discharge slide, all five spindles were again put into operation and a charge of raw ore was fed at the first spindle. The idea of stopping the first three rabbles during chloridizing was to prevent ore from the second zone, which was not roasted enough, from entering the third zone and spoiling chloridizing.

All the raw ore was not fed at one time for this would cool off the furnace too much; one half was fed and the remainder about ½ hr. later, after the first half had begun to ignite.

If the ore, during roasting, had behaved in the same way as the sand with which the movement was studied, the furnace would have worked admirably. But as soon as the ore becomes hot, it flows easily in the furnace, so that, instead of being nearly 8 hr. on its way between feed and discharge, it required less than ½ hr. for raw ore to appear at the last rabbles; therefore, raw ore and nearly roasted ore were constantly mixed; and to obtain a properly roasted charge in the third zone, part of the ore had to remain much longer in the furnace than was necessary and had to be over-roasted in order to roast the raw ore that had just been charged. This not only caused high silver losses through volatilization of silver from the over-roasted ore but decreased the capacity of the furnace until it would not keep its temperature through the combustion of heat of the ore alone, and after drawing off a charge, a small amount of taquia fuel had to be burnt on the hearth of the third zone. The losses of silver were nearly as high as in the McDougall furnace, and the furnace could be considered as an absolute failure. But its operation showed that chloridizing was more rapid and better than in the hand-rabbled furnaces, and that the consumption of salt could be reduced to about 60 per cent. This is to be attributed to the rapid and thorough mixing afforded by overlapping rabbles. The furnace was operated during several months in this way and many plans were tried to improve the results. The speed of the rabbles was varied from ½ to 6 r.p.m., and the rabble teeth were arranged in several ways, but always the ore moved too freely in the furnace and could not be kept in the zone where it belonged according to its state of oxidation. Also considerable ore moved backwards in the furnace, although this should have been impossible on account of the disposition of the rabble teeth, and particles that had been in the third zone were occasionally brought back to the first rabble.

If the furnace had been longer, the ore would have taken more time in traveling from one end to the other, and if it had been possible to experiment with a furnace of fifteen to twenty spindles, the difficulty might

have been overcome altogether. But the erection of such a machine, without the certainty that commercial results would be obtained, was more than the company could afford. Further, although such a furnace might do satisfactory work, the mixture of raw ore with partly and entirely roasted ore would always occur in the first part of the furnace. The ore flows most easily when it has just been ignited; toward the finish of roasting it hardly flows at all, and behaves more or less like cold material. This mixing would always cause over-roasting of part of the ore, causing undue silver losses through volatilization.

MODIFIED FORM OF STRAIGHT-LINE FURNACE

Later, the hearth was divided into three sections and the rabbles of adjoining sections were so spaced that a 6-in. (15-cm.) space was left between the sections that was untouched by the rabbles. A vertical cast-iron sliding door was so arranged between the sections of the hearth

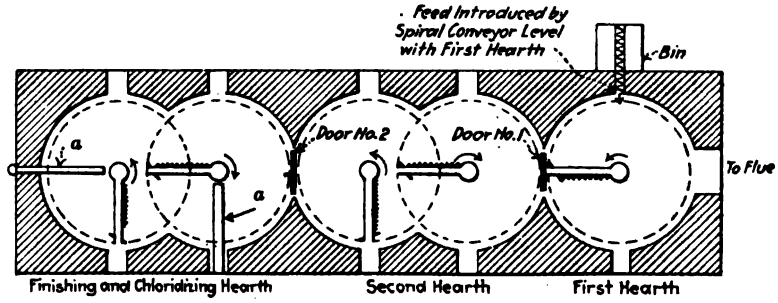


FIG. 2.—MODIFIED FORM OF MERTON FURNACE; *a* IS DISCHARGE SLIDE.

that the ore could pass from one section to the next only if the door was raised, but the door was low enough to let the gases pass freely between it and the arch. In order to facilitate the movement of ore from one section to the other the hearth was stepped 6 in. between each section, the lowest part being the section where the ore was chloridized and discharged. Instead of feeding the ore through the arch, it was planned to introduce it at the center of the first section, or hearth, by a screw conveyor laid in a channel under the hearth and covered by an iron plate. This arrangement, however, had to be altered because the conveyor could not push the heavy ore up the incline at the end of the channel. The conveyor was therefore raised above the level of the rabble and the ore fed at the periphery of the first hearth. This method of feeding was not satisfactory because on the first hearth, which has only one rabble, the ore should be moved from the center to the periphery, whence it is discharged to the second hearth. Therefore the furnace attendant occasionally had to push the ore to the center in order to make it spread more evenly on the hearth surface. In a later design of furnace this trouble has been overcome. This furnace is shown in Fig. 2.

As soon as the furnace got up to its proper temperature, it proved to be a success; it remained hot without the addition of fuel, roasting was uniformly good, and after slight trouble in the beginning, the doors could be operated quite easily. Chloridizing was excellent, and losses of silver through dusting and volatilizing were even smaller than in the hand-rabbled reverberatory furnaces. This was first proved by the higher silver content of the product of this furnace, compared with the roasted ore from the hand furnaces, when both are fed with the same ore. Later, when a lixiviation tank was charged with ore roasted by the new furnace, it was found that the percolation was not as good as usual, which, of course, had to be attributed to a smaller loss of fine ore during roasting. Dust losses in the hand-rabbled furnaces must be considerably larger than in the mechanically rabbled, for the furnacemen generally rabble by making small heaps of ore in one corner of the hearth and then spreading these heaps with a violent push or jerk, which lifts small clouds of dust; but in the mechanically rabbled furnace no dust is caused by rabbling or moving the ore through the furnace.

The operation of the furnace is as follows: After bringing the second and third hearths up to as high a temperature as possible by burning fuel upon them, 700 kg. of ore is fed to the first hearth. If it fails to ignite, some sulfur and oil are introduced through the working door until roasting begins. As soon as the ore has begun to burn in the first hearth, the sliding door to the second hearth is opened, and a certain amount of ore is passed to the second hearth. Every revolution of the rabble pushes a small quantity of ore through the discharge opening to the lower hearth; and as the ore slides and does not fall there is no dusting whatsoever. It is absolutely necessary for the ore on the first hearth to be ignited, because if it is cold it does not flow and moves so slowly that it is practically impossible to transfer a charge of ore to the second hearth. Raw ore is gradually fed to the furnace and, after ignition, is passed farther down on the second and third hearths until there is a full charge of ore on every hearth. From this stage the operation must be carried on carefully and systematically. When the ore on the last hearth is ready to be chloridized, the damper is closed, the necessary quantity of salt is shoveled in at the two working doors, and the charge is chloridized in about 15 min. The discharge slides and the damper are then opened and the chloridized ore is discharged in another 15 min. After closing the slides, door No. 2 is opened and a charge of half-roasted ore is transferred from hearth No. 2 to No. 3, which requires 35 min. Door No. 2 is then closed and door No. 1 opened so that freshly ignited ore from the first hearth is charged on the second; about 25 min. are needed for this operation. Door No. 1 is then closed and the cycle of operations is completed by starting the feeder and introducing raw ore on the first hearth.

Under the conditions described, the capacity of this furnace, which

has hearths of 10 ft. (3 m.) inside diameter, is about 4 tons per 24 hr., when roasting an ore with 30 to 35 per cent. sulfur. The lowest sulfur content at which the furnace can be operated without fuel is 24 per cent., and on such ore the capacity increases to 5.5 tons. The rabbles make 2.2 r.p.m.; if operated at 5 r.p.m. the capacity of the furnace is increased about 20 per cent., but frequent breakage of gears and bearings showed that the construction is not strong enough for the higher speed. Power consumption is 1.8 hp. at 2.2. r.p.m. and 2.6 hp. when running at 5 r.p.m. The operation is simple and easy. All that the work requires is a little attention to the progress of roasting and regulation of draft. The damper is always open just enough to prevent smoke coming out of the two working doors on the third hearth, which are the only openings through which the furnace draws air. A cycle of operations requires no attention but the opening and closing of a few slides and doors, and starting the feeder, which draws its charge from a small bin placed by the side of the furnace. After raw ore is fed on the first hearth, there is nothing for the attendant to do until the charge on the third hearth is ready for chloridizing, which generally takes several hours. Bolivian boys quickly learn to do this work well, and one good man can easily attend to a battery of four furnaces.

Efficiency of Modified Straight-line Furnace

In this furnace 85 sq. ft. (7.8 sq. m.) of hearth area are required to roast and chloridize 1 metric ton of ore with over 30 per cent. sulfur; in the McDougall furnace 58 sq. ft. of hearth are required, but 10 sq. ft. per ton are necessary to chloridize the product in a reverberatory, so that the capacity of the new furnace per square foot of hearth area is 20 per cent. less. If, on the other hand, the modified Merton furnace were built with step bearings to support the spindles from below, instead of suspending them from the framework above, it would be feasible to drive the rabbles at 5 r.p.m. and to obtain a capacity of 5 tons per 24 hr., which would be 1 ton per 68 sq. ft., or exactly the same as the combination of McDougall and hand-reverberatory. But, even if the capacity were considerably lower the quality of work done is so much superior that loss of capacity is not a great objection.

The intermittent system of working, of course, means a certain loss of capacity. The furnace is working at full capacity only when there is a charge of ore on every hearth; therefore, counting from the moment when a charge has been chloridized, it is working on two charges instead of three during 85 min., which is detailed as follows:

	Minutes
Discharging	15
Passing ore from hearth No. 2 to No. 3	35
Passing ore from hearth No. 1 to No. 2	25
Feeding raw ore to hearth No. 1	10
Total	85

One-third of this time, or 28 min., must be considered as lost, since there are only two charges of ore in the furnace; as the time required for one complete cycle is 4 hr., nearly 12 per cent. of the capacity is lost. The difference in time needed to pass a charge of ore from hearth No. 2 to hearth No. 3 and that required to pass it from No. 1 to No. 2 is due to the fact that freshly ignited ore flows more easily than half-roasted ore. Further, the difference in level between hearth No. 2 and hearth No. 3 is 3 in. (7 cm.) less than the height of the rabble teeth. When the ore is being chloridized it piles up in front of the rabbles so that it is pushed against the communication with hearth No. 2, where it is apt to form incrustations which prevent the half-roasted ore from passing freely when the door is raised. These incrustations have to be removed every 24 hr. For this reason the fall between hearth No. 2 and hearth No. 3 should be at least equal to the height of the rabble teeth.

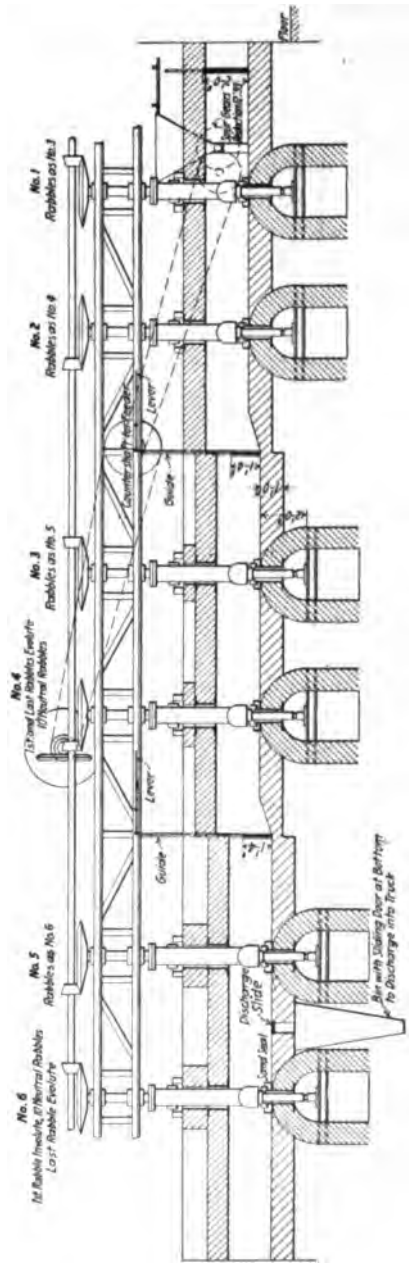


FIG. 3.—CROSS-SECTION THROUGH MODIFIED FURNACE.

In other furnaces of the same type which are now under construction, the spindles are supported on step bearings underneath the hearth, as shown in Fig. 3, and two rabbles are provided for every hearth. The ore is to be fed at the periphery of the first hearth at the first rabble, which has an involute tooth at the end, and will be discharged to the second hearth by the second rabble on the first hearth, which has an evolute tooth at the end. In this way the first hearth will work under much more satisfactory conditions than with only one rabble. The transmission machinery will be so constructed that two speeds are possible, a

slow one, from 4 to 6 r.p.m., to be used during normal operation, and a high one, from 10 to 12 r.p.m., for discharging and moving the ore from one hearth to another. In this way it will be possible to reduce the loss of time perhaps one-half. An attempt will also be made to use two rabbles on every spindle instead of one; this will improve rabbling without increasing the speed.

If a five-spindle furnace running at 5 r.p.m. has a capacity of 5 tons per 24 hr., a six-spindle machine, working under better conditions as far as the first hearth is concerned and equipped with all improvements described, ought to roast at least 6 tons, and probably more. Where larger units are required the furnaces may be built with more hearths, or with hearths of larger diameter. I would prefer the latter, because, if more hearths are used, more time is lost in moving the ore through the furnace. Although the actual time lost is practically the same for a furnace with more hearths, the percentage of time lost is higher on account of the larger number of charges put through the furnace. For instance, assuming that a five-hearth furnace is working under the same conditions as the present three-hearth furnace, it would have a capacity of about $\frac{5}{3} \times 6 = 10$ charges; this means that every 2.4 hr. a charge is drawn off. The time lost between discharging and feeding is:

	Minutes
Discharging	15
Passing ore to hearth No. 5	35
Passing ore to hearth No. 4	25
Passing ore to hearth No. 3	25
Passing ore to hearth No. 2	25
Feeding ore to hearth No. 1	10
Total	135

During this time the furnace would work on only four charges, so one-fifth of the time, or 27 min., is lost, but as the time needed for a complete cycle is 2.4 hr. the percentage of lost capacity is over 18. Further, if a furnace were built with more than five hearths in succession, more time would be needed to move a charge through it than elapses between two chloridizing operations, which means that the ore could not be fed quickly enough and poor chloridizing would result. All this is changed, of course, if the movement of the ore from one hearth to the other is increased by adopting a higher rabble speed.

If, on the other hand, three-hearth furnaces are used with 15-ft. (4.5-m.) hearths, the charges could be made twice as large, say 1500 kg. It should not take more time to transfer a charge of this weight from one hearth to another than a 700-kg. charge in the 10-ft. furnace, because the opening between the two hearths could be made so much wider, say 6 to 7 ft. Therefore, the percentage of time lost, owing to intermittent work,

should not be more than in the 10-ft. furnace, although this question can only be settled by experimenting with a larger furnace.

In furnaces of this kind, it is always necessary to have the two rabbles of one hearth overlap as much as possible so that no dead corners are formed. If an ore contains less than 20 per cent. sulfur, it is not likely that the furnace will keep its temperature, so to avoid the use of fuel the hearths may be built superimposed. During chloridizing and passing the ore from one hearth to the lower one, all draft can be shut off, to avoid loss through dusting, but there is always danger of volatilizing silver because oxidation of the ore, when falling through the furnace, is rapid and gives rise to high local temperatures.

Advantages of Intermittent System

Wherever it is important to obtain a uniform roast, the operation should be conducted in furnaces operated on the intermittent system, as described. If anything goes wrong in a continuous furnace, several hours are required to restore proper working conditions, and in the meantime a product that is not suitable for subsequent treatment must be discharged. In addition to roasting for leaching, this system may be useful when roasting for magnetic separation, or for differential roasting of complex sulfide ores preceding flotation.

As regards the performance of the furnaces, the following figures may be of interest.

Hand-rabbled Reverberatory Furnace

		Kilograms, Silver
Feed.....	15,353 kg. with 1038 gm. silver per metric ton contain	15.936
Product..	12,868 kg. with 1187 gm. silver per metric ton contain	15.274
Difference	2,485 kg.	0.662

The loss in weight during roasting was 16.2 per cent.; the loss of silver 4.16 per cent. Screen tests on feed and product were as follows:

Through Mesh	On Mesh	Feed, Per Cent.	Product, Per Cent.
10	20	14	14
20	40	33	30
40	80	19	20
80	100	6	8
100	150	3	2
150	...	23	25
Tin content.....		2.35	2.74
Sulfur content.....		33.6	2.8
Iron content.....		32.0	39.3
Insoluble inclusive SnO_2.....		26.6	32.8

For chloridizing 4.9 per cent. of salt was used and 2.1 per cent. of fuel was added. The furnace product contained 220 gm. per ton of silver insoluble in water and hyposulfite solution, and lost 6.2 per cent. of its weight by lixiviation, so that $0.938 \times 12{,}868 \times 0.00022 = 2.655$ kg. of silver were lost in the residue. This gives an extraction of 82.6 per cent. of silver from the roasted ore and a total recovery of 79.15 per cent.

Mechanically Rabbled Reverberatory Furnace

		Kilograms, Silver
Feed.....	26,866 kg. with 1119 gm. silver per metric ton, contain	30.063
Product.....	21,690 kg. with 1365 gm. silver per metric ton, contain	29.606
Difference.....	5,176 kg.	0.457

The loss in weight during roasting was 19.3 per cent.; the loss of silver, 1.52 per cent. Screen tests on feed and product were:

Through Mesh	On Mesh	Feed, Per Cent.	Product, Per Cent.
10	20	20	16
20	40	28	27
40	80	18	25
80	100	5	7
100	150	5	8
150		23	25
Tin content.....		2.01	2.38
Sulfur content.....		33.1	3.1
Iron content.....		31.7	38.6
Insoluble inclusive, SnO_2.....		27.8	35.3

Only 3.3 per cent. of salt was used, and no fuel. The residue of the chloridized ore contained 175 gm. silver per ton after leaching, and 4.2 per cent. of weight was lost during leaching, so the insoluble silver lost in tailings was $0.958 \times 21{,}690 \times 0.000175 = 3.636$ kg., or 12.2 per cent. of the silver in the roasted ore. The total recovery is 86.37 per cent. The larger loss of weight during roasting, compared with the hand-rabbled furnace, is due to the smaller percentage of salt used in the mechanical furnace and to the omission of fuel, which contains 45 to 50 per cent. of ashes. Further, the smaller amount of salt used accounts for less soluble salts and therefore for less loss in weight during lixiviation.

No detailed figures need be given for the McDougall and reverberatory chloridizing plant, as the loss of silver in the McDougall alone is over 30 per cent. The McDougall product is never uniformly chloridized and the insoluble residue of the final product is always above 200 gm. per ton on an ore containing around 800 gm. per ton, so the total loss in this system is well over 40 per cent.

The following figures show that nothing is gained by leaving the ore longer in the furnace in contact with salt. After chloridizing a charge, as usual, for 15 min., a sample was taken, and chloridizing continued for another hour, samples being taken at intervals of 10 min.

Chloridizing Period, Minutes	Silver Content of Charge, Grams Per Ton	Insoluble Silver, Grams Per Ton
15	1160	160
25	1200	150
35	1130	150
45	1270	150
55	1260	140
65	1220	150
75	1230	150

The differences in silver content of the charge are due to imperfect sampling, but it can be assumed that once the silver is chloridized no volatilization takes place even if the finished ore is left too long in the furnace. Chloridizing is improved so little by prolonging the process that it is not worth while doing so.

The following figures give a comparison of the cost of roasting in the three different types of furnaces:

	Hand-rabbled Reverberatory	Mechanically Rabbled Reverberatory	McDougall, with Hand-rabbled Chloridizing
Labor	$2.57	$0.52	$0.92
Salt	1.60	1.38	1.41
Fuel	0.40	....	0.17
Repairs	0.05	0.31	0.40
Power	....	0.89	0.73
	$4.62	$3.10	$3.63

These figures are in Bolivian dollars per metric ton; one Bolivian dollar is equal to about $0.36 United States currency. At the time of writing, the improved Merton furnace had been used for over 20 months, and the only repairing due to normal operation was the replacing of several rabble teeth. Since the charge-roasting system puts a much heavier strain on the rabbles than continuous work, all the original gears had to be changed for heavier ones, and rabble arms and spindles were broken in the beginning through the carelessness of operators, whose cleaning tools were caught by the mechanism, but these are not repairs due to normal causes. The rabbles and spindles do not appear to become corroded by the chloride fumes.

Crushing

Originally, No. 4 Krupp ball mills were used, but they were later replaced by two pairs of 36 by 12-in. (91 by 30-cm.) rolls. The rolls did the work for less than one-third of the cost of the ball mills, but gave a

distinctly coarser product which decreased the furnace capacity considerably. Therefore, a Toncap wire cloth of only 0.85-mm. opening was used on the finishing screen instead of one with 1.2-mm. opening on the ball mills, to obtain a product that was suitable for the furnaces. The first rolls were set with a ¼-in. (6.4-mm.) opening and their product went to a trommel with ⅜-in. (9.5-mm.) openings, the oversize being returned to the coarse rolls and the undersize going to the finishing trommel, which was 42 in. in diameter and 12 ft. long. The last trommel was operated in closed circuit with the finishing roll.

Afterwards, a ring-roll mill was installed to do the work of the fine rolls and a 6 by 8 ft. (1.8 by 2.4 m.) Newaygo screen was used instead of the trommel. Although with this arrangement the product was as fine as that from the ball mills and the capacity higher than from the roll plant, it was not found economical, on account of the high power and steel consumption of the ring-roll mill, which also showed other weak points in its construction after having been used for some time. At the time of writing, the rolls are again used, but with a Newaygo screen instead of the finishing trommel; although the product is not quite as fine as that from either ball mills or ring-roll mill, it is sufficiently fine for the purpose. The cloth on the Newaygo screen, which is a No. 8 with 0.078-in. (1.9-mm.) opening, lasts over two months, and the screw conveyor which distributes the the ore evenly over the screen surface has a life of about 75 days. Power consumption is 11.8 hp.-hr. per ton ground from 2 in. (50-mm.) maximum size to about 1 mm., and steel consumption is 0.38 lb. (0.17 kg.) per ton. The following list gives a comparison of products from the different grinding machines used.

Mesh		Krupp Ball Mill 1.2-mm. Toncap Wire Cloth, Per Cent.	Rolls With 0.85-mm. Trommel, Per Cent.	Rolls With Newaygo Separator, No. 8 Cloth, 1.9-mm. Opening, Per Cent.	Roughing Rolls and Ring-Roll Mill With Newaygo Separator No. 6 Cloth, 3.0-mm. Opening, Per Cent.
On	10	3.0	0.0	1.5	4.0
On	20	17.0	19.0	16.0	24.5
On	40	24.0	31.5	19.5	20.0
On	60	8.5	11.0	23.0	5.5
On	80	7.0	10.0	8.0	4.0
On	100	5.0	5.5	5.5	6.5
On	150	3.5	4.5	4.5	9.0
Pass	150	32.0	18.5	22.0	26.5
		100.0	100.0	100.0	100.0

DISCUSSION

P. F. Bliek, Oruro, Bolivia (written discussion).—The first Söhnlein furnace is still working satisfactorily, and the second has been in operation for 8 months; two other furnaces are under construction. The second

furnace has a capacity of ten charges, each of 700 kg. ore, per 24 hr. (7 metric tons), and a hearth surface of 335 sq. ft. The variability of speed in the rabbling, slow for normal operation and fast for the moving of the ore from one hearth to the next, was not applied, as the structure was not sufficiently rigid to stand the strain.

Mr. Söhnlein's principal object was to design a mechanical furnace that could do the same quality of work, regarding losses in silver by volatilization and chlorination, as the hand-rabbled reverberatory furnaces. The results are better; the furnace gives a higher grade of chlorination of the silver and a lower loss in dust and volatilization. However, with the intermittent system of working, considerable time is lost between the moment the chloridized ore is ready to be discharged and the time a fresh charge is loaded on the first hearth. On page 688, Mr. Söhnlein gives that time as 85 min., and calculates a loss of nearly 12 per cent. in capacity. The first furnace is now completing seven charges of 700 kg. per 24 hr., meaning a loss of 13 per cent. in capacity; with the second doing 7 tons per 24 hr., the loss is nearly 20 per cent. Mr. Söhnlein realizes the importance of this loss, but, correctly, does not look for the remedy by increasing the number of hearths; he instead recommends wider furnaces and heavier charges, adding, though, that this problem must be solved by new experiments. The use of wider hearths will increase the capacity of the furnace, but will not lessen sufficiently the time lost in transferring the charges; the use of a thicker layer of ore will retard roasting, which cannot be helped by increasing the number of revolutions of the rabble arms.

In order to mitigate the loss in time by the intermittent system, Mr. G. Herrera, mechanical engineer at the Machacamarca mill, suggested the use of a rabble tooth that, with the normal movement of the rabble arm, brings the underlying ore to the surface; but if the arm is turned in the reverse direction, it gives a positive movement to the ore, transporting it to the periphery. A modification of this kind might reduce by one half the time lost in transferring the charges but it would make the construction of the furnace more complicated though not much more than the two forward speeds suggested by Mr. Söhnlein. These special rabble teeth will be tried in the fourth furnace, now under construction at the Machacamarca mill.

Mr. Söhnlein says that the speed of the rabble arms should be between 2.2 and 5 r.p.m., preferring the higher speed for the increased capacity which resulted in the first furnace. The higher capacity obtained with the higher speed, is not due so much to a faster roasting, as to the quicker transfer of the charges from one hearth to the next. Faster rabbling does not cause faster roasting; on the contrary the roasting time may possibly be increased with an increased number of revolutions. When observing the roasting in a mechanical furnace treating

the high-sulfide Bolivian ores, one might notice that as the rabble arm passes, the hot but dark ore is brought to the surface and in a few seconds is alight. Once lighted, the ore gets brighter, indicating an increased temperature at the surface. This bright color persists generally until the arrival of the next rabble arm. Theoretically, the right moment at which the ore should be stirred again would be just before the surface temperature starts to go down, because if the stirring is done earlier the heat-generating surface ore is buried and the time that elapses before the dark ore brought to the surface ignites again is lost. It is difficult to determine the exact time for a special ore, but with the Bolivian ores it reaches several minutes. A practical example of this was obtained, when operating a McDougall roasting furnace at the Machacamarca mill when temperature and capacity were increased by diminishing the number of revolutions of the rabble arm.

In the Söhnlein furnace, the speed for the ordinary roasting cannot be diminished as long as there is no special provision for a quicker transfer of the ore from one hearth to the other, because the loss in time would increase, but once an arrangement is made for different speeds for normal roasting and for transferring the ore, the first should be kept at two revolutions or less per minute and the second as high as permissible.

On page 679, Mr. Söhnlein refers to the corrosion of the rabble arms in the Kaufmann continuous chloridizing furnace at Huanchaca, caused by the action of chlorine. At Machacamarca, chloridizing was practiced for six months in the McDougall furnace without visible effect on the ironwork; in the first Söhnlein furnace one spindle on the second hearth corroded after 3 years operation, near the water seal, and had to be replaced. Water-cooled shafts and arms will stand chlorine fumes for many years when the atmosphere is dry, and the corroding of the spindle must be attributed to water evaporating from the water seal near the spindle. At Huanchaca, the chloridizing Kaufmann furnaces were working with a layer of chloridized ore that covered the rabble arms and these plowing through the packed chloridized ore corroded rapidly.

The high-sulfide ores develop sufficient heat in roasting to keep the Söhnlein furnace at the required temperature without the aid of fuel. However in the case of ores lower in sulfur, it should be necessary to prevent loss of heat as much as possible; the Söhnlein furnace cools more quickly than the hand-rabbled reverberatories. In the case of ores with not over 20 per cent. sulfur the furnace must be specially designed in order to conserve the heat better.

The loss of heat in the cooling water cannot be neglected. Mr. Wiessing, superintendent of the Machacamarca mill, calculated this loss as 20 per cent. of the heat generated in the second Söhnlein furnace, which uses 20 kg. water per minute; it enters at 25° and leaves at 58° C. Con-

cerning the loss of heat by radiation no data are available, but there is a remarkable difference in the heat conservation between the first and second furnace. In the first furnace the spindles are suspended from the framework, while in the second the spindles have step bearings, accessible through tunnels; these tunnels might be the principal cause of the larger loss of heat by radiation, and for that reason are closed at Machacamarca by a wall of loose mudstones to avoid air circulation. With ores low in sulfur, it might be well to draw off the roasting gases around the furnace or use them to preheat the air.

The principal object in the design of the Söhnlein furnace was to recover more of the silver than could be obtained in the hand-rabbled reverberatory furnaces; so the first cost was a second consideration. The manufacturer charges $8000 U. S. currency for the ironwork of a 7-ton furnace.

The comparison of working costs on page 693 gives an advantage to the Söhnlein furnace, without taking into account the depreciation on each furnace. This should be $0.20 per ton for the hand-rabbled furnace, $0.70 per ton for the McDougall furnace, $1.10 per ton for Söhnlein furnace; all these figures are in Bolivian currency at $0.36 U. S. for $1 Bolivian. Adding these figures to the calculated cost, the difference in working cost is not so manifestly in favor of the Söhnlein furnace; on the other hand the extra gain in silver and the scarcity of skilled labor make this furnace preferable.

Recently the Chocaya mill of the Oploca Co. has installed a Söhnlein furnace of the design and dimensions shown in Fig. 3. Mr. Tonkin, the manager, states that data are available only over a period of six days continuous working. During the first three days, the capacity of the furnace was 3.7 metric tons per 24 hr.; the total loss in silver was 24 per cent., of which 11 per cent. was lost in dust and volatilization and 13 per cent. by unchloridized silver. The ore ran 1390 gm. silver per metric ton, 5 per cent. salt was added, and the loss in weight in the process was 12 per cent. In the next three days the capacity of the furnace was 4.4 metric tons per 24 hr.; a total loss in silver was 20 per cent., of which 12 per cent. was lost in dust and by volatilization and 8 per cent. by unchloridized silver. The crude ore contained 1270 gm. silver per ton, 5 per cent. salt was added, and the loss in weight during the roasting was 27 per cent. No extra fuel was used in the process, and the speed of the spindles is constant at 2 r.p.m. The high loss in silver in dust and by volatilization, Mr. Tonkin attributes to a defective method of feeding.

At the Chocaya mill of the Aramayo Francke mines, there is a 3-ton five-hearth Humbolt furnace with an inside diameter of 11 ft., total useful roasting surface of 300 sq. ft., and outside drying floor on top. Both central vertical shaft and rabble arms are air cooled. At the periphery, the ore slides down from one hearth to the other and in the center

as rapidly as ordinary zinc. The dissolving of pure zinc in dilute sulfuric acid can be greatly accelerated by the addition of a few drops of a solution containing copper or arsenic. The presence of these metals in the solution going to the electrolytic cells would have the same effect on the zinc deposit at the cathodes so that re-solution would set in and might proceed at a rate that would entirely offset the depositing power of the current. In such a case no zinc would result from the passage of the current and nothing but hydrogen would be made at the cathode and oxygen at the anode. Smaller amounts of impurities would result in the zinc being redissolved but more slowly than it is deposited, producing cathodes full of holes of various sizes while the yield per horsepower-day would be proportionally decreased.

Mr. Herbert W. Gepp, who did considerable work with the electrolytic process at Bully Hill, Calif., found that one of the most injurious impuri-

FIG. 1.—BIG FALLS OF MISSOURI RIVER, 12 MI. BELOW CITY OF GREAT FALLS. PROPERTY OF MONTANA POWER CO.

ties present in those ores was cobalt. According to Mr. Gepp and to Prof. G. H. Clevenger, fifteen parts of cobalt per million parts of solution is fatal to electrolysis. The cell work is seriously impaired with only ten parts per million. The cobalt may be precipitated with manganese by the addition of permanganate or it may be thrown down in the presence of manganese by the addition of beta-naphthol and sodium nitrite, also by zinc dust from the neutral solution in the presence of ferric iron, copper and arsenic.

It was not found difficult to maintain an extremely high degree of purity in the zinc solution going to the cells if the iron in the solution was thoroughly oxidized, before being precipitated, by means of limestone or excess calcine and if sufficient zinc dust was added to satisfy fully the copper, cadmium, and whatever small amount of lead might be present. If the ore contains very little iron, in proportion to its arsenic content it

might be necessary to add iron in the form of ferric salt in order to insure the complete precipitation of all arsenic as ferric arsenate. It was found that the best way to make sure of the oxidation of the iron was to maintain a small amount of manganese in solution. Manganese becomes oxidized in passing through the cells, forming permanganic acid, manganic sulfate, and manganese dioxide. The ores contain sufficient manganese for this purpose so that it is seldom necessary to provide outside manganese. It is possible to insure oxidation of the iron by other means notably continued air agitation in the presence of milk of lime.

An aluminum plate made the most suitable cathode and a lead plate the most suitable anode. The latter quickly becomes coated with a brown layer of manganese dioxide and lead peroxide, and if the zinc solution is entirely free from chlorides the lead is not attacked. Some of the lead anodes have been used for three years and seem to be just as good as

FIG. 2.—GENERAL VIEW OF GREAT FALLS 150-TON ELECTROLYTIC ZINC PLANT.

when put in. In the beginning it was the intention to use aluminum plates only for building up starting sheets of suitable weight. This, however, proved unsatisfactory as the starting sheets tended to warp and cause short circuits. Aluminum cathodes are therefore used in all of the cells and the zinc allowed to deposit until a sheet of sufficient weight is built up to go directly to the casting furnace. Generally 48-hr. sheets, which weigh about 20 lb., are made, so that about 40 lb. of zinc is stripped each time the cathode is withdrawn. In order to avoid re-solution, good contact must be maintained between the zinc and the aluminum plate. The plate, therefore, must be roughened sufficiently to insure adherence as the zinc sheet becomes heavier. This limits the weight of zinc sheets it is possible to build up, and this, together with the tendency toward sprouting, limits us to 48-hr. deposits. Seventy-two hour sheets have been successfully made, but on the average the 48-hr. plates give the best results. The better current efficiency with the younger deposits more than offsets

the labor required for more frequent stripping. The experimental work was done with current densities varying from 10 to 100 amp. per square foot. In practice, the most satisfactory density is from 22 to 25 amp. It is not necessary to circulate rapidly as, with the current density used, the evolution of gas at the anode is sufficient to provide the necessary agitation.

The laboratory work at Anaconda was carried on continually for more than 12 months. The solution was used repeatedly, to make sure that nothing would accumulate that might affect the working of the cell. At the same time work was done to determine the effect of various impurities and the degree to which these could be allowed to accumulate without being harmful. At the end of this time it was decided to construct a one-ton plant, but on account of the extremely high selling price of

FIG. 3.—ZINC PLANT, FROM SOUTHWEST, SHOWING LEACHING AND DRYER BUILDINGS, ALSO BOILER PLANT STACK AND TOP OF TANK HOUSE.

zinc, a ten-ton plant was erected. This plant went into commission about the first of November, 1915. By making changes in the various departments, its output was increased to 25 tons per day, and it was operated with considerable profit until Nov. 25, 1916, when the Great Falls plant was able to care for all the available concentrates.

While the Anaconda plant was in an early stage of development it was decided to construct at Great Falls a plant that would be able to produce 100 tons of zinc per day, or 6,000,000 lb. per month. On Dec. 13, 1915, ground was broken for the 100-ton plant and work was pushed as fast as weather conditions would permit. The metallurgical estimates for power were prepared on a basis of 8 lb. of zinc per horsepower-day. Construction work was often ahead of detail drawings and progress in the development of the process called for frequent changes. The type of leaching tank installed was not adopted until February, 1916. The

number of settlers was doubled in March and 50 per cent. was added to the number of filters.

In spite of weather conditions, changes, and delays of material, the most serious being that of the electrical equipment, which was the first of its size ever built, the first unit of the plant began operation on Sept. 11, 1916, and the plant was completed in December. In 1918, the plant was enlarged to make 150 tons per day, or 9,000,000 lb. per month. The plant is of permanent and up-to-date construction throughout; the buildings are brick and steel and all floors are concrete.

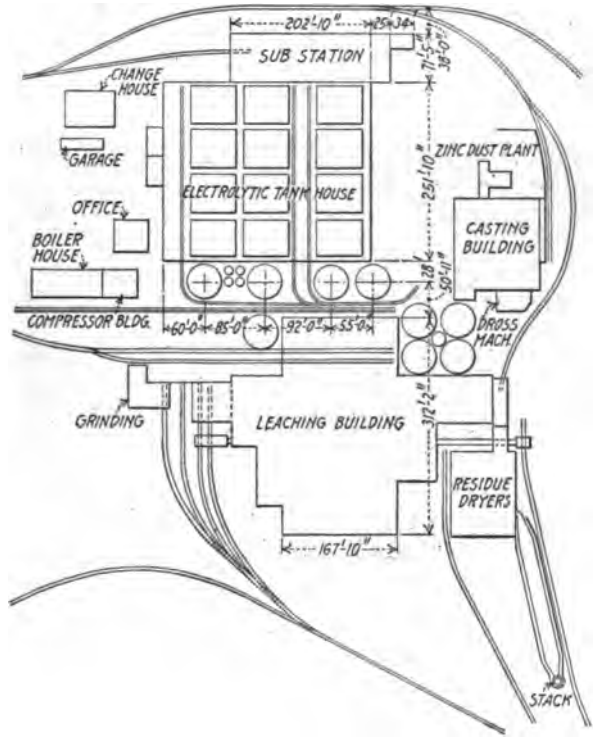


FIG. 4.—GENERAL PLAN OF 150-TON PLANT.

ROASTING DIVISION

The zinc-roasting furnaces are located in the general smelter building, on the north side between the blast furnaces and the reverberatories. There are fourteen roasting furnaces of the Anaconda-Wedge type in two rows of seven each. Each furnace consists of a brick-lined steel shell, 25 ft. in diameter, has seven hearths and one open dryer hearth on top, a 5-ft. (1.5-m.) brick-lined, hollow revolving center shaft which carries 26 water-cooled arms, four for the dryer and first hearths and three for

each of the other six hearths. Each furnace has an individual motor, direct-connected to a series of enclosed reducing gears from which the center shaft is turned by a bevel pinion. The water for cooling the arms is delivered through a water column revolving with the center shaft and connected to the water supply mains by a swivel joint.

The material to be roasted consists of zinc concentrates shipped from Butte and Anaconda in 50-ton, bottom-dump, steel cars and delivered to a battery of fourteen storage bins having a total capacity of approximately 2750 tons, located just under the high-line tracks. From these bins, the material is loaded into 56 cu. ft., V-shaped, rocker-dump cars of 36-in. gage and hauled in trains of eight cars by an 8-ton electric locomotive to individual feed hoppers immediately above the furnaces. Each furnace is equipped with an apron feeder driven by gearing to the revolving cen-

FIG. 5.—GENERAL VIEW OF ZINC ROASTERS IN SMELTER BUILDING, SHOWING LOCATION OF DRIVE MOTORS AND COLLECTING FLUES.

ter shaft, and designed so as to regulate the rate of feed as desired. The rabbles on the arms are so set as to move the material from the circumference to the center of the furnace, and vice versa, on alternate hearths, delivering it finally into the calcine hoppers under the furnaces. From these hoppers the hot calcine is drawn into electrically operated, 4-ton, bottom-discharge larries, hoisted by means of an 8-ton Otis elevator and discharged into revolving coolers, which in turn discharge into a 400-ton storage bin for shipment by the local electric tram to the zinc leaching plant.

Each furnace has two fireboxes, one on each side of the seventh hearth. The fuel used is pulverized Lochray coal, delivered to the roaster storage bin by means of screw conveyors from the coal-pulverizing plant. From the storage bin the coal is delivered by screw conveyor to individual furnace hoppers, each of which is equipped with a feedscrew driven by a

variable-speed mechanism which, in turn, is driven from a central main-line shaft belt driven by an electric motor. The coal is blown into the fire-boxes under 12-lb. pressure through especially designed burners. The ash is passed through grizzlies to launders and sluiced to the river. The gases are carried in cross flues to a main building flue, thence to the uptake and crosstake to the main wire-hung dust chamber, where the dust is settled to be subsequently drawn and re-roasted. The gases pass from the dust chamber, through a connecting flue, to the stack.

This plant was started up, in September, 1916, on the oxide roast as developed at Anaconda when roasting for the 25-ton plant. Sulfate roasting was unsuccessful at Anaconda because there was insufficient draft to keep down the temperature on the top hearth and at the same time burn enough coal on the grates of the fireboxes to maintain the proper temperature in the bottom of the furnace necessary for the elimination of the sulfide sulfur. In December, 1916, when the zinc plant reached full capacity, more acid was required than the acid plant at Anaconda could supply, so it was purchased at a cost of $30 per ton; 30 tons per day were required. It was therefore decided to again try sulfate roasting. The test was begun on the No. 9 furnace; the feed was cut to 30 tons per day and instructions were given to burn enough coal to keep the furnace at 600° C. on the lower three floors with the doors closed and to control the heat on the top floors by means of the doors on the fourth floor and at no time to let the temperature get above 550° C., as shown by a dull red heat. The furnace speed was cut to one revolution per 4 min., which kept the feed in the furnace for 22 hr. The following table gives the results of the test.

Date	Tons[1] of Feed Concts.	Per Cent. Zinc	Hearth Temperatures, Degrees Centigrade					Total Sulfur	Sulfate Sulfur	Per Cent. Soluble Zinc	
			No. 2	No. 3	No. 4	No. 5	No. 6			In H_2O	In 2 Per Cent. H_2SO_4
1916											
Dec. 16–20....	30	34.6	482	521	532	527	541	7.2	5.8	23.3	84.7
Dec. 21–25....	36	35.7	466	516	532	532	549	6.5	4.7	18.1	82.8
Dec. 26–28....	39	35.9	488	516	549	538	555	7.2	5.0	19.5	82.2
1917											
Dec. 31–Jan. 1	42	35.6	493	516	549	560	565	6.5	5.2	20.1	83.3
Jan. 2–5.....	45	35.8	499	510	560	560	565	7.2	4.4	17.3	82.8
Jan. 6–9.....	48	36.6	499	516	565	565	571	5.6	3.5	14.8	82.3
Jan. 10–13....	51	36.4	493	510	555	565	571	6.0	3.6	14.2	80.0

[1]Moisture 8½ per cent.

It was decided, after this test, to put all the furnaces on sulfate roasting with a 40-ton feed, for 32 tons of calcine was needed from each furnace and 20 per cent. indicated water-soluble zinc for that feed

would make the zinc plant about self-supporting on acid. The slow speed of the arms and the low temperature of the sulfate roast resulted in a big reduction in furnace repairs, which more than compensated for the slight increase in fuel and for handling the extra flue dust. Sulfate roasting with its large increase in gas volume approximately doubles the amount of flue dust. Apparently, there is a decrease in silver volatilization with sulfate roasting, because silver recoveries have been much higher at Great Falls than at Anaconda. Various furnace speeds, from one revolution in 80 sec. down to one revolution in 4 min., have been tried. The furnace seems to be less sensitive on the lower speeds and repairs are less, while the solubility and capacity are about the same. The raking has since been changed so that the feed is in the furnace approximately 16 hr. as the roast appeared to be nearly as good at the end of 16 hr. as after 22 hr. By increasing the speed of the concentrate across the floor, the burnout of sulfur was more evenly distributed throughout the furnace and the capacity was somewhat increased. The following table shows how the sulfur is eliminated as the feed passes through the furnace; the samples were taken after the calcine had crossed the designated hearth. The sulfur elimination is faster than indicated because the roasting concentrate is constantly decreasing in weight for the calcination approximately 90 per cent.

Hearth	Per Cent. Sulfur	Approximate Grams of Sulfur Eliminated per 100 Gm. New Feed
Dryer Hearth	35.4	
1	28.8	6.6
2	22.6	6.2
3	16.8	5.8
4	10.6	6.2
5	6.4	4.2
6	4.8	1.6
7	2.8	2.0

Much has been said about the difficulty of roasting zinc concentrates to render the zinc soluble in the presence of considerable iron. It was found that insoluble zinc compounds are undoubtedly formed and the percentage of zinc that remains insoluble increases as the roasting temperature becomes higher. However, it is not difficult to make a calcine containing 82 per cent. of its zinc in soluble form in 2 per cent. H_2SO_4 from a concentrate that contains 33 per cent. zinc to 20 per cent. iron, and we hope to increase the percentage of soluble zinc to 85 per cent. A concentrate containing 50 per cent. zinc and under 5 per cent. iron will yield a calcine containing about 94 per cent. of its zinc in soluble form.

On the other hand, if the temperature is allowed to get too high, the soluble zinc may be as low as 60 per cent. for a 33-per cent. zinc concentrate. Just what is the most suitable temperature depends on the concentrate undergoing treatment. In general, roasting should be done at between 600° and 625° C., although on low-iron concentrates the temperature may be greatly increased if the concentrate does not sinter, as will happen if the percentage of lead is high.

The 1918 extension called for more roaster capacity than was available at Great Falls. Fourteen of the 20-ft., six-hearth, McDougall furnaces in the copper-leaching plant at Anaconda were therefore converted into zinc roasters. They are the standard Anaconda McDougall and are equipped with flotation concentrate link-belt feeders, Cottrell dust collectors, fireboxes on the sixth hearth, Anaconda calcine coolers,

FIG. 6.—LARRY CAR UNDER CALCINE HOPPERS OF WEDGE ROASTERS, ALSO LARRY ON ELEVATOR GOING TO CALCINE COOLERS AND CALCINE STORAGE.

and a conveyor system for the delivery of concentrate from the zinc concentrator to the roaster feed hoppers and from the coolers to standard railway cars for shipment of the roasted concentrate to Great Falls. These furnaces have given better and more consistent results than the larger Wedge furnaces. The Cottrell treaters, being placed just over the furnaces, precipitate sulfur trioxide with the flue dust, which is returned hot to the first hearth of the furnace, when the treater plates are rapped. This sulfur trioxide appears to combine with the moisture of the incoming concentrate, forming sulfuric acid on the first hearth, and produces a fuming effect; this may account for the increase in the amount of soluble zinc. Experiments have shown that the solubility of the zinc in roasted concentrates can be greatly increased if the raw concentrates are moistened with sulfuric acid before roasting. Solubilities of 85 per cent. have

been consistently made in these furnaces when the same material only yielded an 82 per cent. solubility in the larger furnaces at Great Falls.

Roasting Zinc Concentrates

Following is an average of the daily assays of calcine produced, from low-grade concentrates, at the zinc roasters, Anaconda, during June, 1919; also, the average results in September, 1918, at Great Falls.

RESULTS OBTAINED IN 20-FT. MCDOUGALL FURNACES AT ANACONDA

			Concentrate	Calcine
Zn, per cent	34.5	Zn, per cent	31.9	34.5
Total S, per cent	4.1	Cu, per cent	1.6	1.7
SO_4S, per cent	3.5	Pb, per cent	9.0	10.0
Sol. Zn, per cent	85.67	Ag, ounce	16.0	17.6
Furnaces operating	12.22	Au, ounce	0.06	0.07
		Insoluble, per cent	6.0	7.0
		FeO, per cent	19.0	21.0
		S, per cent	34.0	4.1

RESULTS OBTAINED IN 25-FT. WEDGE ROASTERS AT GREAT FALLS

			Concentrate	Calcine
Zn, per cent	33.0	Zn, per cent	30.5	33.0
Total S, per cent	4.5	Cu, per cent	1.8	1.9
SO_4S, per cent	3.7	Pb, per cent	9.5	10.3
Sol. Zn, per cent	82.7	Ag, ounce	16.5	17.8
		Au, ounce	0.06	0.07
		Insoluble, per cent	6.5	7.4
		FeO, per cent	20.0	22.3
		S, per cent	34.5	4.5

SOME OF THE ZINC CONCENTRATES ROASTED AT GREAT FALLS

	Cu, Per Cent.	Zn, Per Cent.	Pb, Per Cent.	Ag, Ounces	Au, Ounces	Insol., Per Cent.	SiO_2, Per Cent.	FeO, Per Cent.	Al_2O_3, Per Cent.	CaO, Per Cent.	As, Per Cent.	S, Per Cent.
Anaconda zinc concentrates	1.83	34.0	7.25	11.9	0.074	5.8	4.9	18.9	3.7	0.1	0.38	35.1
Childers zinc concentrates	1.01	31.7	12.0	6.6	0.049	8.6	6.0	15.2	2.9	0.7	0.32	29.6
Nelson zinc concentrates	0.30	45.7	1.4	20.3	0.010	5.8	4.2	8.5	3.0	3.7	0.14	26.7
Greenhill Cleveland	0.27	37.2	8.1	16.3	0.010	10.8	9.5	14.2	5.2	0.1	0.19	22.2
Highland Surprise	0.10	33.6	9.0	4.3	0.012	16.6	14.2	14.5	3.1	0.1	0.32	24.0
Rex	0.90	31.4	14.98	5.9	0.008	14.4	11.8	13.7	3.6	0.1	0.22	23.6
Success	0.14	31.1	8.0	4.7	0.007	27.2	21.3	10.7	4.7	0.8	0.22	19.5
Midvale	1.71	33.2	9.86	8.6	0.052	11.0	8.3	13.1	11.8	1.1	0.32	28.2
Hercules	1.60	37.4	9.73	17.8	0.014	5.0	3.7	16.0	7.0	0.1	0.29	25.3
Pilgrim Fuller	1.13	34.4	3.3	15.1	0.190	12.0	9.7	16.5	3.7	0.1	2.91	28.6
Standard Silver & Lead	0.33	43.2	1.26	19.0	0.015	7.4	6.0	9.1	2.9	4.1	0.19	25.1
Colorado	1.88	45.7	4.01	9.5	0.020	3.0	2.1	11.8	1.7	0.1	0.54	34.3
Federal	0.17	38.2	8.57	7.4	0.010	9.0	7.0	12.0	3.3	0.1	0.51	21.8
Butte & Superior	0.55	52.4	3.8	19.5	0.030	9.2	7.8	3.5	....	0.2	....	29.6
Elm Orlu	1.45	51.3	3.5	16.3	0.035	5.3	4.2	6.5	....	0.2	....	32.0

Notes on Theory of Roasting for Zinc Leaching

1. It was recognized at the beginning that ore or concentrates must be finely pulverized to get the maximum solubility; the following screen analysis shows the fineness of the concentrates being treated at Great Falls.

	Per Cent.
On 50 mesh	0.10
Through 50 mesh on 60 mesh	0.53
Through 60 mesh on 120 mesh	13.33
Through 120 mesh on 200 mesh	18.93
Through 200 mesh	67.11
Total	100.00

Purchased material, when appreciably coarser than flotation concentrates, is sent through the ball-mills. This serves the double purpose of pulverizing the concentrate and thoroughly mixing it with the mill concentrates, giving a uniform feed for the roasting and leaching plants.

2. The low initial temperature of the roast gives better solubilities on concentrates containing appreciable amounts of lead and iron sulfides. Lead, if 5 per cent. or more is present, tends to cause the roasting concentrate to sinter and ball up at the higher temperatures; as these agglomerated masses will be insufficiently roasted, poor solubility results and a larger amount of classifier sand is produced in the leaching plant.

The aim is to prevent the simultaneous oxidation of the iron and zinc, as far as possible, by keeping the temperature of the two top roasting hearths below the active break-up temperature of zinc sulfide and yet high enough to permit FeS_2 and FeS to oxidize in the time allowed. Unfortunately, zinc sulfide begins to oxidize at the low temperature of the upper hearths but to a less degree than the iron sulfide, therefore a small amount of ferrate will be formed. If zinc dross containing a large amount of metallics is fed in with the concentrates, even at the low temperature of the top floors, the formation of ferrates is greatly increased. If the dross is charged to the lower floors, where there is little or no iron sulfide, there is very little formation of ferrates.

3. The amount of sulfate formed is dependent on a low initial temperature, so that apparently the amount of sulfate formed is largely influenced by the amount of Fe_2O_3 present and the reactions that take place in sulfate roasting are those of the contact acid process, where freshly prepared ferric oxide is used as a catalyzer. The iron sulfide is oxidized to ferric oxide in the top hearths and acts as a catalyzer changing the sulfur dioxide from the roasting zinc sulfide to sulfur trioxide which, in turn, combines with the freshly forming zinc oxide to form zinc sulfate. In proof of this, if the temperature at first is high, practically all of the iron will be combined with the zinc to form ferrates, in which case

very little sulfate will be formed although temperatures and sulfur elimination are the same in the lower part of the furnace as when sulfating.

4. The amount of sulfate remaining in the finished calcine is dependent on the end temperature. To decrease the percentage of sulfate sulfur, it is only necessary to raise the end temperature and break up or prevent the formation of sulfates. While the solubility falls when the sulfates are broken up, it will be better than when ferrates are formed on the top hearths instead of Fe_2O_3.

5. More time is required for sulfate roasting, which means that the capacity will be less and the fuel consumption greater.

6. The gas volume is greater when sulfate roasting, so that more flue dust is produced. The excessive amount of air needed for cooling is responsible for the increased gas volume.

7. The function of the auxiliary heat from the fireboxes is to maintain the oxidation temperature of the roasting concentrates in the lower floors and to heat the air that supplies the oxygen and carries away the sulfur dioxide on the lower floors. The volume of gas from the fireboxes must be relatively large for sulfate roasting, otherwise the temperature will be so intense that the sulfate will be broken up in passing through the drop holes and in front of the fireboxes.

8. The capacity of the furnace at Great Falls is limited by the temperature of the second hearth. For instance, the radiation and the amount of heat carried out in the cooling water are constant, therefore the oxidation of more sulfur and iron on this floor will cause an increase in temperature to a point where the zinc sulfide begins to break up. But if more air is admitted for cooling, dusting will be excessive.

9. The SO_2 in the gas from the furnace intake is 2 per cent. or less for maximum solubility when running the furnace at capacity. We think this is a coincidence rather than a necessary condition. The function of the big excess of air is cooling, otherwise the capacity of the furnace would be the same both summer and winter; as a matter of fact, the furnaces have a greater capacity in winter than in summer while the concentration of SO_2 is higher and the amount of soluble zinc the same.

CUMULATIVE RECOVERY OF GREAT FALLS ROASTER PLANT FROM SEPTEMBER, 1916, TO DECEMBER 1, 1919

	PER CENT.
Zinc	98.169
Copper*	100.661
Gold	98.042
Silver	95.749
Lead	95.680

* The amount of copper is small, 1.50 per cent., and is reported to hundredths.

The accompanying table shows the recovery of the roaster plant at Great Falls. About 90 per cent. of the concentrates came from Anaconda, where they were weighed and sampled. The losses include the

loading, transit, and unloading losses as well as the stack loss. The Great Falls stack and flue system leave little to be desired from a dust-settling standpoint.

Leaching Division

The leaching is continuous and is carried out in two steps: (1) A neutral leach where all the calcine and approximately one-half of the total acid is added; (2) an acid leach where no calcine and the remainder of the acid is added.

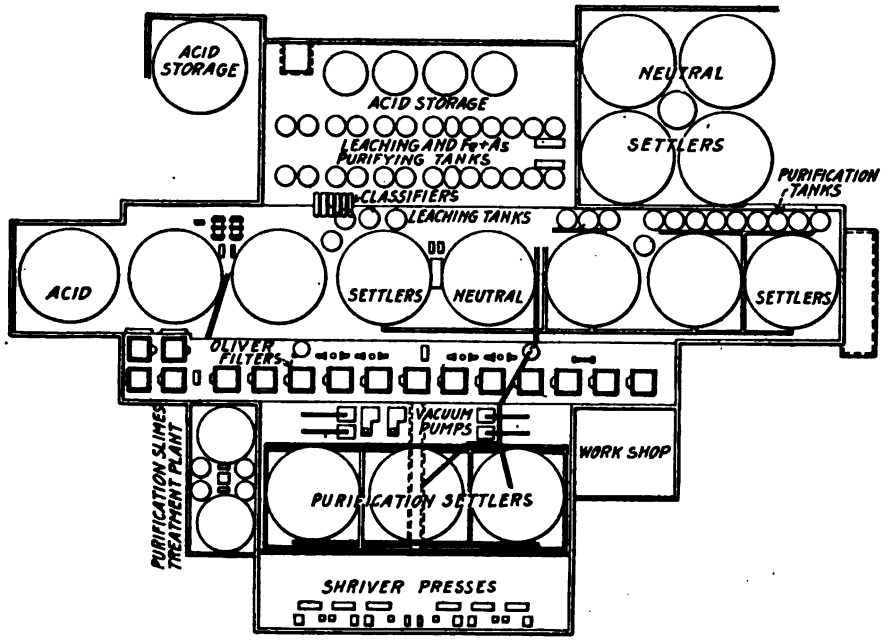


Fig. 7.—General plan of 150-ton leaching building.

The solution for the first, or neutral, leach is made up with one-half of the cell acid (11½ per cent. sulfuric acid and 2½ per cent. zinc) and the partly spent leach liquor (0.6 per cent. sulfuric acid and 10 per cent. zinc from the acid leach). This mixture is run into the first of a series of seven continuous leaching Pachuca tanks. Sufficient iron must be present and oxidized to account for all the arsenic and antimony, otherwise they will not be removed and poor tank-room efficiency will result.

Calcine is run into the three succeeding Pachuca tanks in such a manner that there is an average drop of 2½ per cent. acid in each tank. Nothing is added to the fifth tank, as it is used as an indicator, or control, tank in which the acid should be nearly, or completely, spent. One-sixth of the total amount of calcine is added to the sixth Pachuca tank

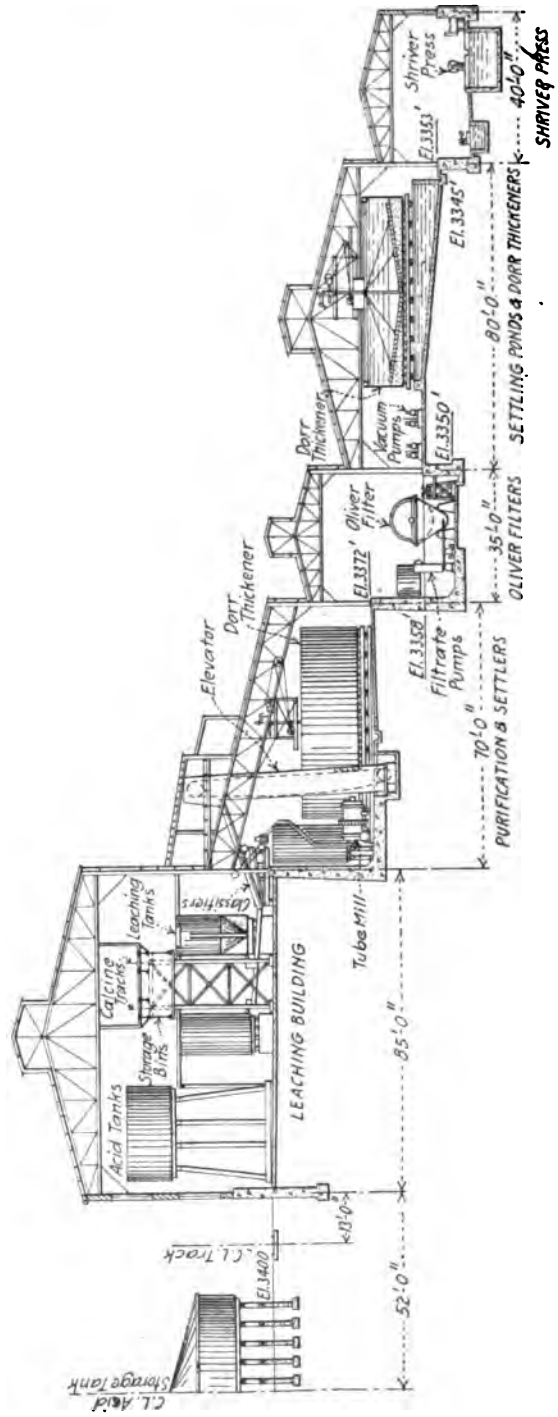


FIG. 8.—CROSS-SECTION THROUGH LEACHING DIVISION.

together with a small amount of pulverized limestone. The excess base contained in the calcine and lime rock completely precipitates the ferric iron, granulates the gelatinous silica, and partly precipitates the copper. These chemical precipitates, together with the insoluble residue, carry down the freshly formed insoluble compounds of arsenic and antimony and completely free the solution from them. For instance, the arsenic may be as high as 2 gm. per liter in the liquor in the third Pachuca tank and less than 1 mg. in the liquor of the seventh Pachuca, which is also a

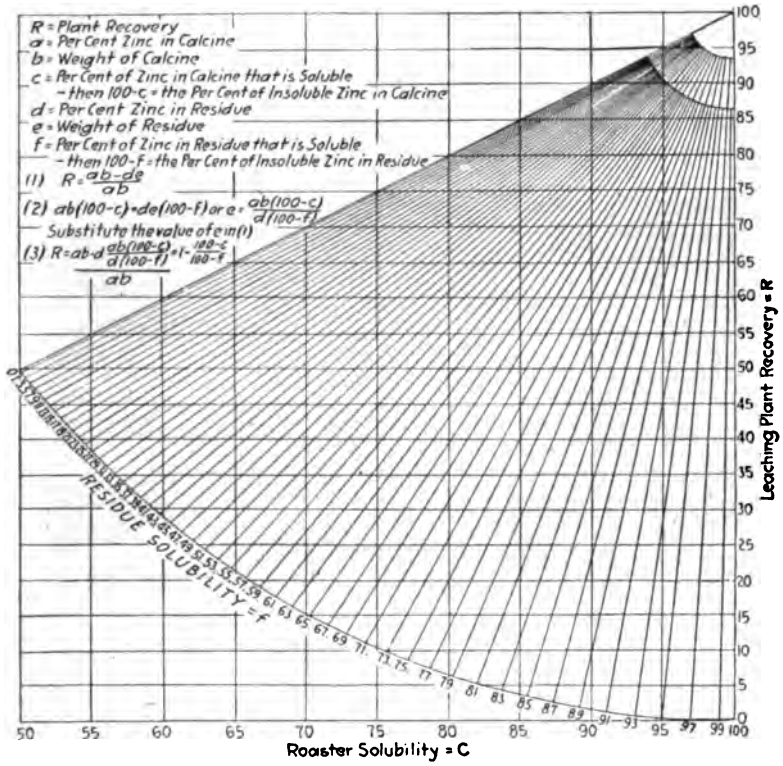


FIG. 9.—GRAPHIC PRESENTATION OF ZINC-PLANT RECOVERY FORMULA, BASED ON FACT THAT INSOLUBLE ZINC IN CALCINE EQUALS INSOLUBLE ZINC IN RESIDUE.

control tank, but its function is mostly physical. After the base is added it takes several minutes for the leach to coagulate. If this step is carried out too rapidly, poor settlement results and in a short time the rest of the plant will be blocked with mud. When this step is properly carried out each granular particle of solid appears to be enclosed in a flake of freshly precipitated iron, lime, or gelatinous silica; that is, each solid particle becomes a nucleus about which the chemical precipitate collects and provides the necessary weight to carry down these flaky particles. The capacity of the settling equipment is dependent on the proper

handling of the seventh Pachuca. It is easy to control but requires close attention.

The discharge of the last Pachuca goes to the neutral classifiers. These take out the sands, which are reground and returned to the system for further treatment. The overflow from the classifiers flows to Dorr settlers, which discharge a clear overflow for the purification tanks and a spigot product, containing 50 per cent. solids, which forms the feed to the acid leach.

To sum up, in the first, or neutral, leach: (1) All the calcine enters the process and approximately three-fourths of the soluble zinc is taken into solution. (2) The iron is oxidized and precipitated. (3) Gelatinous silica is coagulated by excess base and rendered granular. (4) The arsenic and antimony are completely precipitated. (5) Eighty per cent. of the copper is precipitated as hydroxide by the excess base; this

FIG. 10.—LOCATION OF CONCRETE PONDS, VACUUM PUMPS, OLIVER FILTERS AND DORR SETTLERS.

makes possible the cheap removal of most of the copper and supplies the iron for the removal of arsenic and antimony in the acid leach. (6) A large percentage of the zinc is separated from the residues and is contained in a clear settler overflow along with 20 per cent. of the soluble copper and all the soluble cadmium which goes to the purification plant, while the settler spigot product containing three parts of solids and two parts of solution is elevated to the acid leach. The only heat used in the process is that supplied by the chemical reactions and electric current in the tank room.

The ground neutral classifier sand and the neutral settler spigot product are leached in three 10 by 20-ft. (3 by 6-m.) continuous leaching Pachuca tanks with the remainder of the cell acid and sent to the acid settlers. This operation is simple; it is necessary only to see that the overflow from the Pachucas is maintained at approximately ½ per cent.

acid. Variations of 1 per cent. over a considerable time do not materially affect results, but too high an acid for a long period increases the volume of solution, hindering settlement, and causes the iron to circulate, which interferes with the settlement of the neutral side. Too low an acid for a long period results in low recovery due to undissolved ZnO and to high moisture in the filter cake caused by precipitating ferric hydroxide, gelatinous silica, and alumina without granulating. Poor settling of the acid settlers also results for the same reasons.

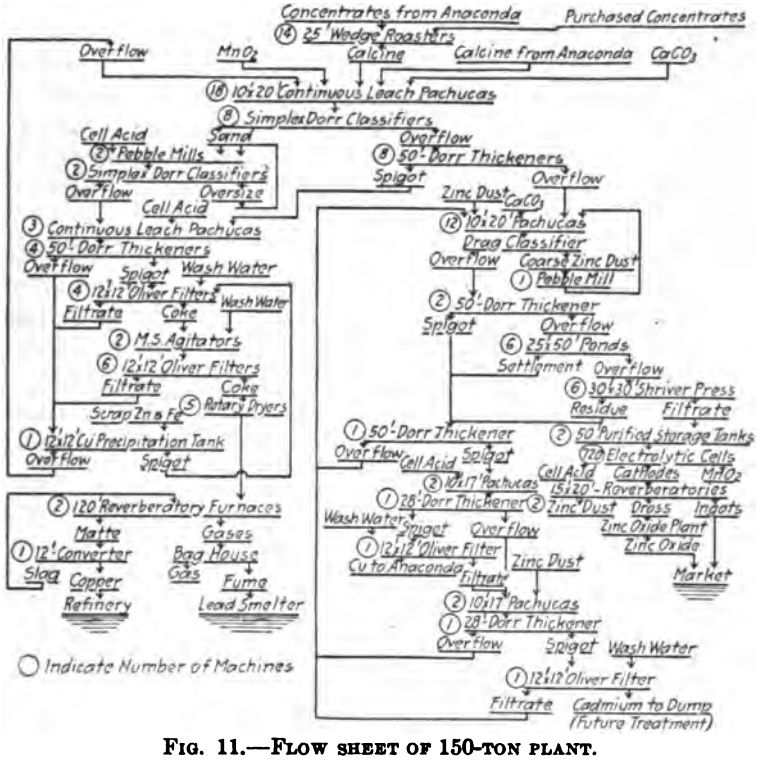


FIG. 11.—FLOW SHEET OF 150-TON PLANT.

The spigot product of the acid settlers, containing 60 per cent. solid and 40 per cent. moisture, goes by gravity to blanket-covered filters of the Oliver type. The cake from these filters is repulped with hot water or hot water and acid, in case there is enough acid-soluble zinc left in the first cake to justify it, and then refiltered on a second set of blanket-covered Olivers to recover more of the soluble zinc. Hot wash water is used on each set of filters. If this double filtering operation is properly carried out, less than 20 per cent. of the zinc contained in the residues will be soluble in dilute sulfuric acid. In other words, if 90 per cent. of the zinc in the calcine was soluble, 10 per cent. of the total zinc in the calcine would be in the final residue as insoluble zinc and

would be 80 per cent. of the total zinc in the residue. That is, the recovery would be 87½ per cent. (Graphic solution, Fig. 9.) We consider this good practice and easily obtainable on 45 per cent. zinc calcine.

The filtrate from the acid filters is combined with the acid settler overflow and goes to the copper roughing tanks where scrap zinc from the tank room and scrap iron are added to rough out the copper. It is then pumped to the first of the neutral leach Pachucas and forms a part of the neutral leach acid.

The results of the acid leaching system are: (1) Solution of the remainder of the acid-soluble zinc and the copper; (2) final separation of the solids from the zinc and copper solutions; (3) roughing out of the copper and chlorine; (4) solution of sufficient iron to guarantee the removal of arsenic and antimony in the neutral leach step; (5) elimination of the arsenic and antimony which are only partly redissolved in dilute acid. (About 10 per cent. of the arsenic and antimony circulate in the acid Dorr overflow.)

Fig. 12A shows approximately how zinc and associated impurities go into solution in the first, or neutral, leach, reaching a maximum at approximately 2.5 per cent. acid and how iron, arsenic, alumina, and soluble silica are precipitated by excess calcine over that required to neutralize free acid, again partly dissolving in the acid, or repulping, leach. The solution used in the first leach is a mixture of acid settler overflow and cell discharge solution. A number of parallel leaches were made under exactly the same conditions, taking one for each point on the curve and analyzing the solution to obtain the results as plotted. After adding the varying amounts of excess calcine, the pulps were allowed to settle for 2 hr. and the clear solution was carefully decanted, leaving a thickened pulp containing approximately one-third of the total solution. The decanted solution was taken for the data plotted in C and the remaining pulps were used to obtain the data plotted in B.

Fig. 12B is a presentation of the results obtained in the repulping, or acid, leach. The data were obtained by carefully adding fresh cell-discharge solution to the pulps containing excess calcine, taking one leach for each set of results. This curve shows how the amounts of iron, arsenic, antimony, and alumina returned to the neutral leach may be controlled by regulating the acid content of the repulping leach discharge. The results, as plotted, are higher than would be obtained if only the precipitated impurities were releached, as some of the impurities in solution are obtained from the excess calcine added in the neutral leach. Precipitated silica dissolves only slightly, if at all, in the repulping leach; yet some is contained in the solution from this leach, having been dissolved from the excess calcine.

Fig. 12C illustrates the copper and cadmium purification, using zinc dust. The clear solution from the neutral leach pulp was treated with

increasing amounts of zinc dust to obtain the data shown. The curves are borne out in practice, but do not show the true order in which copper and cadmium are precipitated. They show that most of the copper is eliminated before cadmium is precipitated, but cadmium is eliminated in almost the same ratio as copper when zinc dust is first added, but quickly redissolves precipitating copper from solution. When copper is practically completely precipitated, a large part of the cadmium remains in solution and requires a large excess of zinc dust over the theoretical for its complete removal. This excess zinc dust is recovered and used to pre-

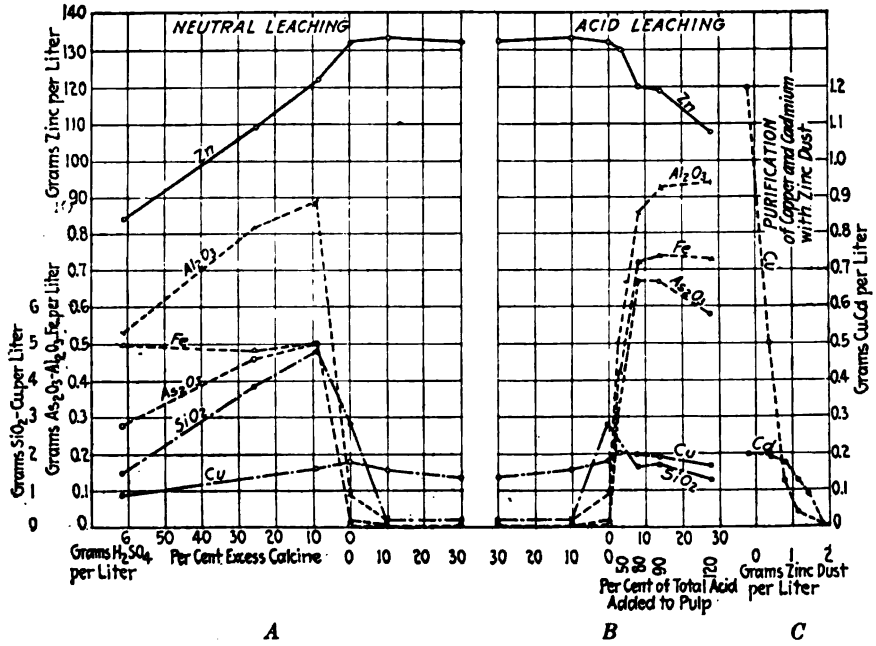


FIG. 12.—GRAPHIC REPRESENTATION OF THE CHEMISTRY OF (*A*) NEUTRAL LEACHING AND PRECIPITATION OF As_2O_3, Fe, SiO_2, AL_2O_3; (*B*) ACID LEACHING OF THE THICKENED PULP FROM *A*; (*C*) ZINC DUST PURIFICATION OF THE CLEAR SOLUTION FROM *A* FOR Cu AND Cd.

cipitate copper from a second batch of solution. An overall efficiency of 80 per cent. of the zinc dust added is considered good practice; the other 20 per cent. is partly recovered in the purification slime treatment plant by leaching with dilute acid solution.

If zinc dust is added to a clear solution of copper and cadmium sulfates and only slightly agitated for a few minutes, the bright zinc dust is black and spongy. If the solution is filtered, it will be found that copper and cadmium have been eliminated in about the same proportions. If the agitation is continued and there is insufficient zinc present to precipitate all copper and cadmium, the color of the residue will change to red

or reddish-brown and the solution will contain a much smaller proportion of copper to cadmium than the first sample. If only 50 per cent. of the zinc dust required to precipitate the copper is added, the second sample will contain a higher actual percentage of cadmium than the first. In practice, the purification operation is carried to completion, so the reaction between metallic cadmium and copper sulfate is completed. Under certain conditions the precipitated cadmium will redissolve if allowed to remain in contact with the purified solution.

The presence of ferrous sulfate seems to be especially harmful; it is evidently oxidized to ferric sulfate, dissolving the finely divided metallic cadmium. Long-continued aeration of solution containing ferrous sulfate and precipitated cadmium will redissolve some or all of the cadmium. A trace of free acid will also redissolve precipitated cadmium.

Copper Precipitated by Scrap Iron

When the excess of calcine, made necessary by the adoption of the continuous leach system, was added, it was found that a large part of the copper was precipitated in the neutral leaching tanks and settlers. This copper again went into solution when the neutral spigot product was releached, causing trouble in the purification plant because it built up in the leach cycle. At times, when sufficient calcine to precipitate the copper was not added, the copper in the neutral Dorr overflow would suddenly increase as much as 100 per cent., so if sufficient zinc dust to precipitate it was not added, the tank room suffered. When it was found that copper was being concentrated in the Dorr overflow, the solution of the problem was easy; the copper in the acid Dorr overflow was precipitated with scrap iron until enough iron was in solution to take care of the arsenic, then the rest of the copper was precipitated with scrap zinc from the tank room. Formerly it was the practice to dissolve the scrap zinc and iron in the cell acid storage tanks. A tank 12 ft. (3.6 m.) in diameter by 12 ft. deep was fitted with an air-lift agitator and used to dissolve the iron and scrap zinc for precipitating the copper. In this tank sufficient scrap iron and zinc were added to guarantee the desired result. The adoption of this scheme effected material saving of zinc dust in the purification plant.

PURIFICATION

The failure of the early experimenters to recognize the harmful effects of minute quantities of certain impurities is the principal reason for their disappointment. It is not safe to say that a definite amount of any impurity such as copper, arsenic, antimony, cobalt, cadmium, tellurium, or selenium can be tolerated because the toxic effects of most of these appear to be cumulative. For instance, when a small amount of copper is

present (10 mg. per liter), the harmful effect of a little arsenic or antimony is greatly multiplied, therefore the only safe thing is to eliminate all to the greatest possible degree. If the neutral leach is properly carried out, the neutral Dorr overflow will contain, in addition to zinc sulfate, all the soluble cadmium and a certain percentage of the copper; but the arsenic, antimony, ferric iron, and part of the copper will have been precipitated. The final purification with zinc dust will take care of the copper and cadmium and will precipitate a certain amount of any arsenic and antimony that has passed the neutral leach; but it is not safe to depend on the zinc dust for arsenic and antimony removal.

The Great Falls purification plan is based on the fact that a large excess of zinc dust will completely precipitate the last traces of cadmium and copper; therefore, to get a reasonable efficiency from the zinc dust, a recovery system was installed and later supplemented by a purification slime treatment plant. Copper is rapidly removed by the zinc dust but cadmium is removed slowly and with difficulty unless a large excess of zinc dust is used. As cadmium must be reduced to less than 20 mg. per liter in the purified solution, to make grade "A" zinc in the tank room, and as no rapid test of which we are aware is sufficiently delicate to indicate that small amount of cadmium, it has been necessary to develop the present practice.

Operation of Purification Tanks

The overflow from the neutral settlers is pumped to twelve 10 by 20-ft. (3 by 6-m.) air-agitated Pachuca tanks, where it is treated; first, with recovered zinc sludge from the purification classifiers, to rough out the copper, then with zinc dust, added carefully until copper cannot be detected with the hydrogen-sulfide test. A definite excess of zinc dust is then added to insure that all cadmium is precipitated. The amount of excess dust added is determined by practice and is varied from day to day by the zinc-plant superintendent after he has received the analyses of the neutral Dorr overflow and the purified solution for the previous day. It is a cut-and-try method but is not difficult to control. Like the rest of the process it must be carefully watched because an error here results in poor tank-room efficiency for several days. The best method is to avoid trouble by using plenty of dust. On the other hand, the use of too much dust is expensive, but so long as there is insufficient zinc sludge coming back from the classifiers to rough out the copper too much zinc dust is not being used.

After the addition of the excess zinc dust, the tank is agitated for 15 min. and then discharged through a drag-line classifier to two 10 by 50-ft. (3 by 15-m.) Dorr settlers in parallel, which are in series with six 25 by 65-ft. concrete settling ponds. The ponds are arranged in parallel, so

that any one can be cut out for cleaning without interfering with the others, and are 7 ft. (2.1 m.) deep at the feed end and 2½ ft. at the discharge; the sloping bottom facilitates cleaning. During normal operations one pond is sluiced out per shift, if the sludge is allowed to remain in the bottom of the pond too long, the cadmium oxidizes and goes into solution. Traces of acid or ferric sulfate hasten the re-solution of the cadmium. The pond overflow launder leads to a concrete sump, which supplies the feed to eight Shriver clarifying presses. The purified solution, after passing the presses, is as clear as crystal. If the overflow from

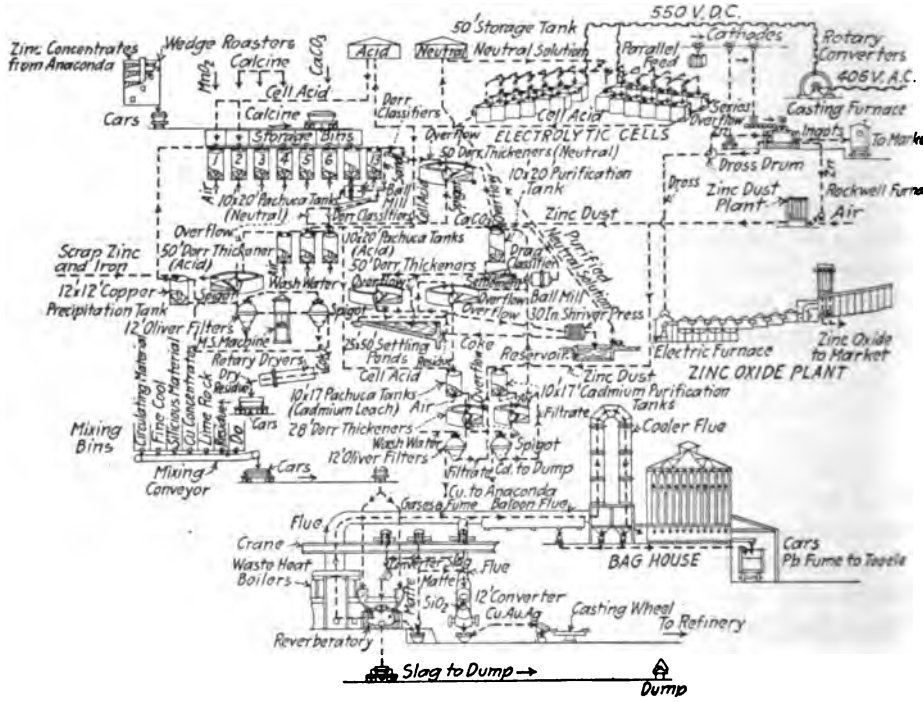


FIG. 13.—FLOW SHEET OF 150-TON PLANT.

the ponds is clear, the presses are probably superfluous, but they act as a safeguard and all the solution has been forced through them. The clarified solution is pumped to two 12 by 50-ft. (3.6 by 15-m.) storage tanks and forms the feed to the tank room. The sludge from the purification Dorrs and the ponds is pumped to a scavenger Dorr, which receives all the spill and washings from the presses and the purification settling system and acts as a combination settler and slime storage tank for the purification slime treatment plant. The overflow of the scavenger settler is pumped back to the purification tanks. The spigot product of the scavenger settler is the feed to the purification slime treatment plant.

Operation of Purification Slime Treatment Plant

The scavenger spigot product is pumped to two 10 by 17-ft. (3 by 5.1-m.) leaching Pachuca tanks until they are about one-third full, then cell acid (10 per cent. sulfuric acid) is run in slowly while the tanks are agitated until copper begins to go into solution (sodium-sulfide test.) At this point, the zinc and cadmium are in solution while the copper is still in the solid state. These leaches are now pumped to the copper settler, where the copper is collected in a rich slime, 30 per cent. copper in the spigot product, and is filtered on a 12 by 12-ft. Oliver filter and sent to Anaconda to the copper smelter. The overflow of the copper settler contains the cadmium and zinc and is run to two 10 by 17-ft. Pachuca purifying tanks, to which fine zinc dust is added in sufficient quantity to reduce the cadmium content of the solution to that of the neutral Dorr overflow. After the cadmium is precipitated, these tanks are discharged to a 10 by 30-ft. cadmium settler, the overflow of which goes back with the scavenger settler overflow for purification. The spigot product of the cadmium settler contains 12 per cent. cadmium and is to be treated for the recovery of metallic cadmium. Approximately 500 lb. of cadmium per day is contained in this product. The process for the recovery of cadmium has been worked out and the plant will, most probably, be installed when the demand for cadmium justifies it.

Electrolyzing Division

The tank house contains 864 cells divided into six electrical, or solution, units. The cells are 10 ft. 3 in. (3.12 m.) long, 2 ft. 10 in. (0.86 m..) wide, by 5 ft. (1.5 m.) deep. They are made of wood with a lead lining and are bolted together with heavy, 3/4-in. (19-mm.) iron bolts at the end. Each cell contains 28 anodes and 27 cathodes. The cathodes are approximately 2 ft. by 3 ft. 6 in. by 3/16 in. thick and have a copper contact bar riveted on the top so that 3 ft. of the cathode is submerged; they are spaced 4 in. on centers at right angles to the solution flow. The anodes, made of chemical lead, are so cast that the lead completely encloses the copper contact bar except at one end, where contact is made with the conductor bar. The anodes are slightly smaller in cross-section than the cathode but are 3/8 in. thick. They are spaced 4 in. on centers in such a way that the distance from the cathode to the anode is approximately 1 3/4 in. The triangular conductor bar used permits all of the contacts to be on the outside of the cell nearest the aisle. This allows easier inspection and cleaning and makes it unnecessary for the workmen to lean over the tank and breathe the fumes that rise from the solution undergoing electrolysis.

Each tank-room unit, or block of 144 cells, is subdivided into 24

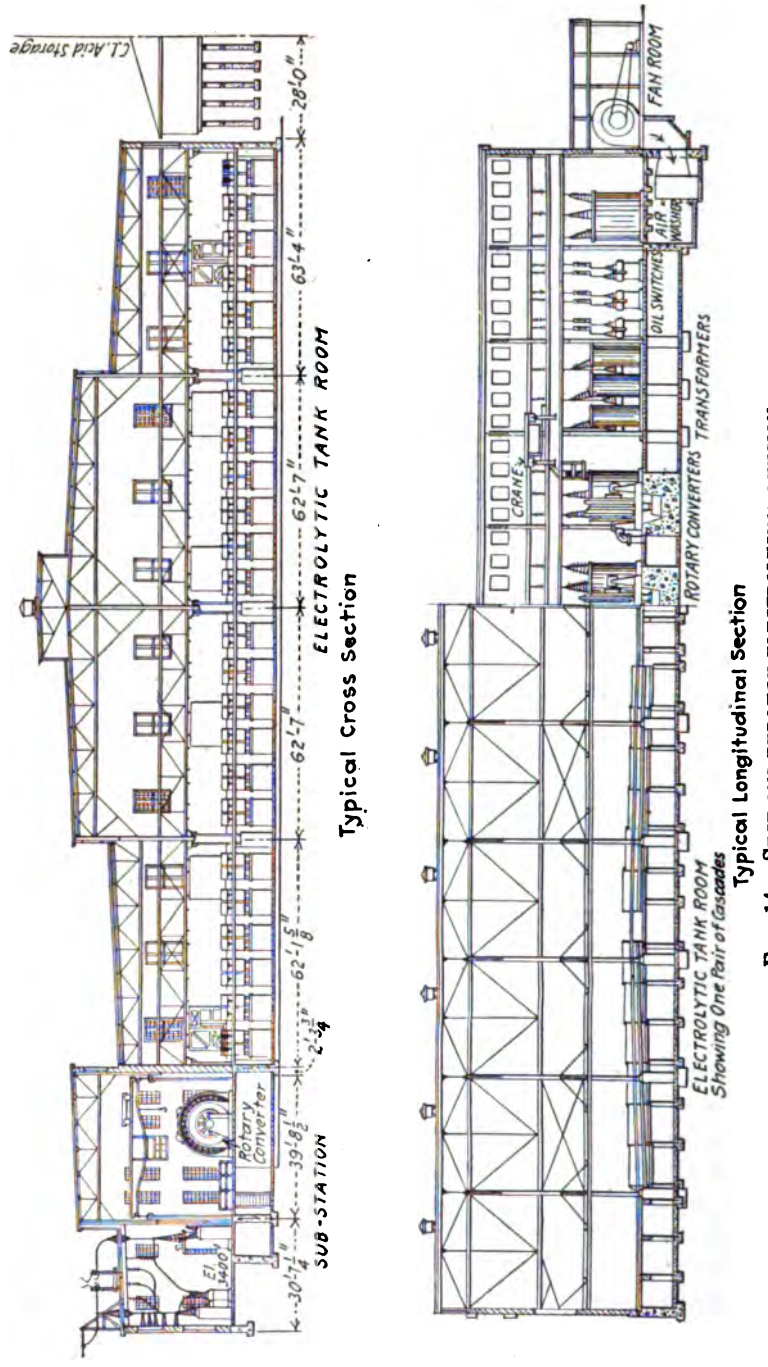


FIG. 14.—SECTIONS THROUGH ELECTROLYZING DIVISION.

cascades. Each double cascade forms a stripper unit, which is divided by a runway. The cells of each cascade are placed end to end so that the discharge of the top cells flows into the next lower cells. The discharge of the sixth cell spills into the tail launder, which carries the spent electrolyte to the acid discharge storage tank. The feed solution is brought in by 6-in. (15-cm.) lead mains from the purified storage tanks and is distributed to the cells by iron feed pipes. Each double cascade has an individual feed pipe with a valve control so that the solution can be fed to any cell in the system. Solution is fed into the first five cells of a cascade; the sixth cell is used as a control from which hourly samples are taken and run for acid. The system used is really a parallel feed and a series flow of solution through each cascade. The 6-in. lead lines are broken and connected with 6⅝-in. rubber hose to prevent current grounds.

Electrical Units

The current for each electrical unit of 144 cells is supplied by a rotary converter of 5800 kw. output at 580 volts and 10,000 amp. maximum capacity. At full load, the current density is approximately 30 amp. per sq. ft. The voltage and, indirectly, the current may be varied 40 volts up or down by means of a booster set. Each additional 1000 amp. on a circuit calls for a raise of approximately 15 volts on the circuit. The 80-volt range with the booster set permits a decrease of over one-half the amperes without changing the transformer taps. Whenever necessary, the internal resistance, that is the resistance of the electrolyte, can be changed by increasing or decreasing the acidity of the electrolyte. The drop across a cell is 3.8 volts when operating with 10 per cent. acid and 10,000 amp. As the cells are in series, this means that the over-all voltage is over 500 volts. It is only possible for a workman to get one-half of this voltage because the neutral of each circuit is connected to the ground. This arrangement has proved very satisfactory. The plant has been in operation for over four years and no trouble has been experienced from this high voltage.

The first 5800 kw. rotary, after being run several hours with no load, was ready for operation on Sept. 10, 1916. As this was the largest machine of this type, the electrical superintendent decided to have it come in on as small a load as possible, therefore the cells were only partly filled with solution to decrease the plate surface. It was also arranged for the rotary to receive current from a special generator at the power house. In other words, it was not dependent on the synchronous booster set for voltage regulation. The power was switched on the first unit at 9:20 a.m., Sept. 11, but very little current flowed owing to the high resistance of the neutral solution and the high current density due to the partly filled cells; these were filled as soon as possible.

LOG OF A UNIT STARTING UP

Head solution 85.5 *G. P. L. Zn*

Time	Switchboard		Cell		Temperature, Deg. C.	Remarks
	Volts	Amperes	Volts	Per Cent. Acid		
11	510	1000	3.54	1.0	..	No flow.
12	510	1200	3.54			
1	510	1500	3.54	1.4	30	
2	510	2000	3.54			
3	515	2500	3.57	1.8	..	Small flow on head cells.
4	515	3250	3.57			
5	515	3300	3.57	2.4	40	
6	515	4000	3.57			
7	515	4500	3.57	2.7		
8	515	5000	3.57			
9	515	5500	3.57	3.4		
10	510	6000	3.54			
11	510	6500	3.54	4.1		
12	500	7000	3.47	...	50	Small flow on all cells.
1	495	7000	3.44	4.4		
2	490	7000	3.40			
3	480	7000	3.33	5.3		
4	478	7000	3.32	...	..	Regular flow on all cells.
5	478	7000	3.32	6.0		
6	475	7000	3.30			
7	475	7000	3.30	6.3		
8	470	7000	3.26			
9	475	7000	3.30	6.9		

The tank room was started up with green men, except one man per shift who was trained in the 25-ton plant at Anaconda. The second unit was started Oct. 14, and came in much faster because cell acid from the first unit was added to each cell to cut down the resistance, also we were not afraid to push the rotary to the voltage limit.

The individual cell feed tried in the Anaconda plant was perfected and adopted. This made possible a close acid and voltage control of the tank room without excessive supervision because the flow of each cell was small and small changes were at once apparent to the eye. The hourly acid control samples from the end of each cascade act as a check on the inspector's judgment. The appearance of the solution, the size of the gas bubbles, and the degree of the pungent odor of the acid mist help in detecting abnormally high acid cells. If the zinc is allowed to become nearly depleted in any cell the hydrogen gas will take fire and small, rapid explosions result.

The yield per horsepower-day was over 10 lb. (4.5 kg.) and the zinc deposited was nearly ideal until about the first of December when it

began to show signs of surface corrosion. The character of the deposit gradually changed until its resemblance to the arsenic deposit of the test cell could no longer be mistaken; but the chemists reported no arsenic in solution. At last, it was decided to apply the arsenic cure (adding scrap iron to the cell acid return launder). The effect was apparent within 24

FIG. 15.—PARTLY ASSEMBLED CASCADE, SHOWING ANODES IN PLACE, INSULATOR BETWEEN CASCADE SOLUTION DISCHARGE PIPE AND RETURN SOLUTION LAUNDER, ALSO GRATING FLOOR BETWEEN CASCADES. SMALL TRACK IN FOREGROUND IS FOR ZINC CATHODE CARS. NOTE OVERHEAD TROLLEY ARRANGEMENT.

hr. and re-solution completely stopped within a week. It has since been the practice to add scrap iron whenever strong acid was being added to the system; during this time 30 tons per day of chamber acid was required.

1917	Average Daily Tons Cathodes Produced	Amperes per Sq. Ft.	Current Efficiency	Pounds Zn per Horse-power-day	Average Monthly Analysis of Ingots			
					Per Cent Cd	Per Cent Fe	Per Cent Pb	Per Cent Total
January.....	95.7	20.8	87.55	11.681	0.036	0.0088	0.0163	0.0611
February.....	87.1	19.7	88.63	12.300	0.0293	0.0094	0.0153	0.0542
March.....	100.1	23.5	85.71	11.595	0.0318	0.0096	0.0224	0.0638
April.....	100.0	20.5	82.4	11 15	0.0127	0.0081	0.0220	0.0428
May.....	100.17	22.2	82.8	10.83	0.0371	0.0094	0.0286	0.0451

The results obtained in the cell room during the first five months of 1917, after the addition of scrap iron was standardized, are given in the preceding table.

Care of Tanks

The solution flow for each unit of 144 cells is looked after by one inspector on each shift, who sees that each cell gets the proper supply of solution and glue, looks out for leaks and poor contacts, and samples the spent electrolyte of each of the 24 cascades once per hour. These samples are titrated with standard sodium-carbonate solution, using methyl orange as an indicator, and the results recorded in the log book. Variations of over 1 per cent. are rare. It is possible, by close attention, to have each cell discharge contain the same percentage of acid. To lessen the work and to be sure of sufficient zinc in solution in all the cells, the acid in the last cell is higher than in any of the preceding cells in a cascade.

On day shift, twelve tank men do the stripping of the metal for each unit; that is, each tank man tends one stripper unit, one-half of which he strips each day. The cathodes are stripped every 48 hr. and produce two sheets of zinc, each weighing from 15 to 20 lb. (6.8 to 9 kg.), which are stacked on small 20-in. (50-cm.) gage, ball-bearing cars and delivered over the casting-plant scales at the end of the day's shift. In addition to stripping the metal, the tank man keeps his unit in shape; he is responsible for the cleanliness and general condition of the cells, aisle, and equipment. He is paid a bonus based on quantity of zinc produced. Good tank men earn from 25 cents to one dollar per day more than the common laborers.

Nine cathodes are removed at one time and placed in a rack, resembling a display rack, which permits the stripping of adjacent sides of two plates each time that one cathode is swung to the side. The cathodes are washed with hot water and surfaced with a wire brush when needed. The anodes are cleaned once each month or six weeks. The zinc sheets are not washed before they are sent to the melting furnace.

The tank room is in charge of a department superintendent, who has a stripper foreman and three head inspectors under him. The stripper foreman has charge of the tank men and repairmen and looks after the stripping of the metal and the general condition of the tanks and equipment. The head inspector has charge of the inspectors and the solution supply; he is a change-shift man.

Every workman employed in the tank room is furnished daily with a piece of antiseptic gauze large enough to fold and make a nose and mouth mask of eight thicknesses; this mask is held in place by an elastic band. It is the duty of the tank-room foreman to see that every workman wears a mask while in the tank room. As the gas bubbles, in leaving the solution, atomize a small amount of the electrolyte, there is at all times a mist

of this dilute sulfuric acid and zinc-sulfate solution in the air. The mask completely filters out this mist.

A clothing allowance of $1.75 per week is paid each tank man for the deterioration of clothes and gloves.

All floors are made of wood and in addition are insulated from the tanks, bar lines, and ground. The steel building columns, to the height of a man's head, are boxed in with wood. Chain blocks have a strain insulator between them and the crawl. As an added precaution against electric shock, shoes with non-conducting rubber or wood soles are furnished to all men employed in the tank room.

A first-aid man is in attendance during the stripping period; the men are encouraged to go to him for the dressing of all minor cuts and scratches. Zinc-sulfate solution, due to its astringent action, causes bad sores, if neglected. There are no indications of the development of any occupational disease.

FIG. 16.—STRIPPING OPERATION, SHOWING STRIPPING RACKS AND PLATFORMS, LIFTING FRAMES, WOODEN STRIPS ON CATHODE EDGES TO PREVENT BUILDING OF METAL OVER THE EDGE, CATHODE CARS, NOSE MASK, STRAIN INSULATOR BETWEEN CHAIN BLOCK AND CRAWL, ETC.

Deterioration of Aluminum Cathodes

When the gas leaves the surface of the cell, it atomizes a certain amount of the acid electrolyte, part of which comes in contact with the exposed surface of the aluminum plates. As these are relatively warm, the water evaporates leaving a concentrated acid which causes a constant deterioration of that portion of the plate above the solution level. When aluminum sells at 50 cents per pound, the aluminum cost approximates 75 cents per ton of zinc deposited. So far we have been unable to find a coating that will resist the acid for any length of time. Welding was suggested as a possibility, but it has been impossible to satisfactorily

weld two pieces of plate aluminum. Aluminum plates ¼ in. (6.35 mm.) thick were tried, as it was thought they would last enough longer to pay for the extra weight of aluminum, but there seems to be a difference in the hardness and uniformity of aluminum plates over 3/16 in. thick. It was found that ⅛ and 3/16-in plates stood the stripping while the ¼-in. plates became rough, causing the zinc to stick and the aluminum to peel off with the zinc; so it was necessary to scrap all the ¼-in. plates before they showed signs of corroding above the solution line.

FIG. 17.—DAILY CATHODE PRODUCTION ON CARS.

Anodes

The first lead anodes were cast about 1 in. square copper conductor bars, so that the anode contact could be bolted down if necessary. These large bars nearly covered the surface of the cell when the cathodes were in place and caused the cell to heat unless a large amount of cooling water was kept in circulation. The atomized acid corroded the projecting ends of the copper bar and crept between it and the lead covering, forming a deposit of copper sulfate that, in time, completely destroyed the contact between the lead and copper. New anodes were made by casting the lead completely over a ⅜ by 1¼ in. (9.5 by 31.7 mm.) copper anode bar and cutting away the lead on one end so that the conductor bar made contact with the copper of the anode bar.

Glue

Between 1 and 1½ oz. (28 to 42 gm.) of glue per ton of metal produced, depending on the amount of impurities in the electrolyte, has been added at 2-hr. intervals since the plant has been in operation. When re-solution appears, the amount of glue is increased. Glue low in chlorides should

be selected, otherwise the loss due to anode corrosion will be greater than the gain from the use of glue. The judicious use of glue gives a dense deposit resulting in better melting recoveries of zinc.

Manganese Dioxide

Manganese dioxide is deposited at the anode and falls to the bottom of the cell, which was designed with storage space on the bottom to hold the accumulation for 6 mo., which is the life of the wooden insulators.

Insulation

Originally, dry maple blocks, dipped in hot paraffin, were used to support the conductor bars and dead ends of electrodes; glazed tile has been found preferable whenever it can be used without crushing. The current loss due to leakage to ground is small if proper attention is paid to insulation. All wood insulators must be replaced at least once in every 6 mo. when the cells are being cleaned of manganese dioxide. Strain insulators were placed between chain blocks and the trolley, so as to prevent a leakage to ground when the lifting racks come in contact with the cathodes.

Impurities

Copper.—In minute amounts, 10 mg. per liter of solution or less, copper does not appear to have much effect on the zinc deposit. In larger amounts, holes are eaten through the cathodes, leaving a black deposit on the aluminum surface; at times a bright deposit of copper is obtained. A second deposition of zinc will not take place until the aluminum sheet is thoroughly cleaned of the black deposit. If copper is the only injurious impurity present, the zinc deposit where not corroded will be firm and bright. High acids are conducive to active corrosion of the impure copper-zinc deposit. Copper attacks the surface of the aluminum sheet which becomes so smooth that zinc will not adhere until it has been resurfaced.

Antimony.—This is the worst impurity. The presence of any amount that can be determined (one part per 1,000,000) will give a very low current efficiency and a badly sprouted deposit, which results in low melting recovery. The deposit, when held to the light, shows a network resembling a lace curtain and is lifeless, retaining any form into which it is bent without even partly recovering its original form. The presence of antimony in the zinc deposit has not been detected although present in the electrolyte in appreciable quantities.

Arsenic.—The presence of 1 mg. of arsenic per liter in the electrolyte will make itself known at the end of 30 or 40 hr. in a type of cathode

corrosion peculiar to arsenic. The surface of the deposit becomes rough in appearance and loses its luster. As this condition proceeds corrugations develop. Larger amounts of arsenic give a badly sprouted deposit similar in appearance to that caused by antimony. After completely re-dissolving the zinc deposit from a portion of the aluminum surface, a second period of deposition will begin, and as many as four depositions have been noticed for a single 48-hr. period.

Iron.—The presence of iron in the electrolyte in moderate amounts does not injure the current efficiency, although when oxidized it causes the aluminum cathode sheets to deteriorate rapidly and, therefore, it should be oxidized and precipitated in the neutral leach and not allowed to overflow the neutral settlers. During the month of February, 1917, from 25 to 30 tons of chamber acid were added to the plant solution. The acid contained approximately 500 mg. of arsenic per liter; it was necessary to add scrap iron to insure arsenic removal. The iron in the purified solution at times was over 0.2 gm. per liter; it averaged 0.13 gm. per liter for the month. Sufficient iron was oxidized in passing through the cells to provide the necessary ferric iron for arsenic removal. The electrolyte was of a greenish color throughout the cell system and apparently no permanganic acid or manganese dioxide was formed as only about one-half of the iron was oxidized. After a month's trial, it was decided that, due to the deleterious effect of the iron on the aluminum cathodes, the continuous use of the high iron was not justified, although the plant averaged 89.3 per cent. current efficiency and yielded 12.3 lb. per d.c. horsepower-day for the month. The aluminum cathodes showed marked corrosion at the solution line and along the edges.

Manganese.—Manganese, in the absence of other impurities, has little, if any, effect on the zinc deposit. In the higher states of oxidation, as it exists in the cell, it aids re-solution of the deposit when started by other impurities. Pure zinc will dissolve more rapidly in cell solution than in pure dilute sulfuric acid, owing to the oxidizing effect of the manganese. Where cobalt is present in solution, it is claimed by other experimenters that at least a portion of the cobalt is precipitated by the manganese dioxide in the cell. It is also claimed that manganese protects the lead anodes from corrosion and that the deposit of manganese dioxide is beneficial. We insist that this manganese dioxide deposit must be removed at least once every six weeks.

Cadmium.—The presence of 0.6 gm. per liter of cadmium in the electrolyte does not injure current efficiency or the character of the zinc deposit. To make grade "A" zinc, the cadmium must be under 20 mg. per liter in the purified solution.

Chlorine.—Chlorine, in some forms, attacks the anode very violently when present in amounts of 50 mg. per liter or more. The cathode deposit does not appear to be affected by it.

Nitrates.—Nitrates are undesirable as regards anode corrosion, especially in the presence of chlorine. The cumulative effect of the two is worse than either one alone.

Cobalt, Nickel, Tellurium, Selenium, Etc.—These have not been investigated sufficiently to warrant definite statements. Sodium and potassium have no deleterious effect in moderate amounts when present as sulfates.

Temperature.—The corrosive effect of impurities increases greatly with the temperature. Since any re-solution causes an increase in temperature, and an increased temperature hastens re-solution, it is sometimes hard to tell which is the cause and which the effect. With slightly impure solution, it is possible to maintain a fair current efficiency if the temperature can be kept down; this suggests the use of more cooling coils. With pure solution, a moderate rise in temperature, say from 35° to 70° C., does not cause a falling off in efficiency or change the character of the deposit; more effort should be spent in purifying the solution instead of providing extra cooling.

Solids in Suspension.—If the solid in suspension is a conductor, such as manganese dioxide or carbon, it will cause sprouting of the cathode metal. The electrolyte should be clarified before going to the cells and all foreign matter should be kept out of the electrolyte. When the cells become foul with manganese dioxide, so that it is in suspension, sprouting is more prevalent than at other times. The sprouting is always more intense on the bottom of the cathodes, where there is a higher concentration of the suspended particles.

Addition Agents.—It has long been the practice in electrolytic copper refining to add moderate amounts of glue at regular intervals. At the suggestion of Mr. Willis T. Burns, glue was tried and found to be beneficial. Too much glue causes brittle metal, starts re-solution of the zinc deposit, and may prevent the deposition of any zinc; the addition of moderate amounts will greatly retard sprouting and give better current efficiency, especially when small amounts of arsenic and antimony are present. After the addition of glue, there is a slight voltage rise and the gas bubbles from the cathode deposit greatly increase in size; probably due to a change in the character of the surface film of the electrolyte. Glue appears to make this film tougher so that the bubbles of gas hang on to the sprouts and raised spots for a longer period, partly insulating them. The low places in the deposit appear to build up faster, giving a much denser deposit with glue than without it. The effect of the glue on the electrolyte only lasts for a short period. Evidently the glue is decomposed, because during periods of re-solution when an excessive amount of gas is coming off it must be added more often. With pure electrolyte, the addition of glue is not necessary. Like Mr. C. A. Hansen, we feel that the effort should be made to purify the electrolyte, instead of doping it.

Sugar, wood juice, starch and a number of other agents give approximately the same results but glue is the most trustworthy and cheapest.

Melting Division

The zinc-casting plant contains two coal-fired reverberatories with a capacity of from 100 to 125-tons per furnace and one electric furnace with a daily rated capacity of 200 tons. After a six-month's trial the use of the electric furnace was discontinued for the following reasons: (1) When melting zinc cathodes, the dross formed coats over the surface of the metal, preventing the transfer of heat to the bath. (2) It is impossible to get nearly the full production without volatilizing considerable metal; with a production of 170 tons per day, over 3½ per cent. of the zinc charged is volatilized. (3) The metal bath cools during charging so that heat is required in the muffles to keep the metal hot enough for casting. (4) At 70-tons capacity the furnace compares very favorably with the coal-fired furnaces, but when the investment is considered the furnace is a failure for zinc-cathode melting. (5) The heat in the resistor troughs is so intense, when melting 100 tons per day, that the trough construction will not stand up, causing frequent long delays for repairs. The work of this furnace confirmed the laboratory experiments, that when zinc cathodes are melted they will produce a definite amount of dross. To get a good melting recovery the dross must be worked to separate the metal from the oxide.

Coal-fired Reverberatories

Zinc cathode sheets are apt to be porous to a certain extent and one side is covered with sprouts or raised spots. There is also a coating of zinc sulfate. Even when melted in a covered crucible, from 4 to 5 per cent. of dross is formed. This dross contains metallics and may be reduced 40 or 50 per cent. in weight if worked hot with ammonium chloride. The best recovery of the metal over a month's operation was 96½ per cent.; 3½ per cent. of the metal went to form dross, which assayed 83½ per cent. zinc, showing that approximately one-sixth of it was metallic.

The zinc-melting reverberatories are made of common brick below the metal line and of firebrick above. To avoid metal leakage the whole furnace is set in a sheet-metal pan, which is supported by I beams set on concrete piers. This construction permits air cooling of the bottom. The main chamber of the reverberatories is built rather high so that there is a deep bath of metal and a big stack of cathodes at all times; this gives a large surface of metal exposed to the heat. The melting zinc running down the surface of the stack carries away the dross and always presents a new surface of bright metal to the hot gases from the firebox, which

is large and deep. It is operated as a partial gas producer so that the resulting gases will be reducing, to avoid oxidation of the metal. The dross from the melting cathodes is carried down with the molten zinc and floats on the top of the bath, gradually slowing up the furnace. At intervals this dross is rabbled with ammonium chloride, which causes the particles of molten zinc to combine and sink into the bath. Once every 24 hr. the dry dross is completely removed from the furnace and further worked, while hot, in a revolving cement mixer, to which oil and ammonium chloride are added. The addition of a small amount of oil and sawdust to the dross helps to keep up the temperature. Approximately 50 per cent. of the zinc contained in the furnace dross is recovered as metal in this way. This metal collects in the bottom of the cement mixer and is tapped out through a hole into molds.

Charging

The loaded cathode cars are brought to the charging stand over which there is a one-ton electric hoist, which places 4 or 5 tons of the cathodes upon a roller coaster. This conveys the metal to the charging doors in the top of the furnace; when the charging door is swung open and the brake on the roller coaster released the bundle of cathodes slides into the furnace. It is only necessary for the furnace to be open a few seconds while charging. Every precaution is taken to exclude the air from the furnace while melting; all openings are sealed except during the dross-skimming period. The furnace is allowed to cool down about 150° C. before opening it to skim the dross.

Casting and Sampling

The molten metal is dipped from metal sealed dipping muffles and poured into 50-lb. (22.6 kg.) slab molds of which there are 40 in line with each muffle. The dipping ladles hold over 200 lb. of molten zinc and are carried from an overhead crawl. Each is operated by one ladleman who has a helper to mark and stack back the slabs from the molds. A crew of eight men does all the weighing, docking, and loading of the metal.

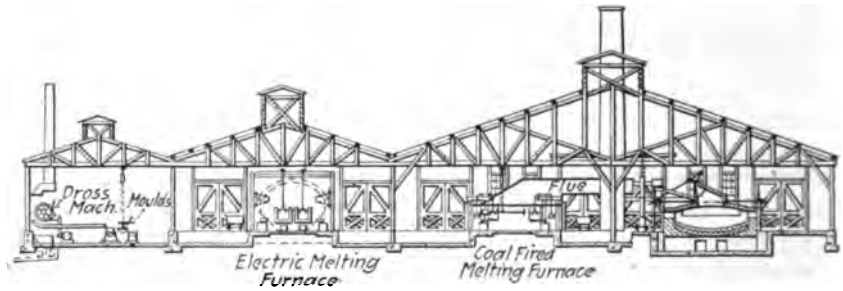
A sample of metal is taken from every twentieth ladle and cast in pencils in a split graphite mold; these pencils are broken up and combined to form the sample representing each day's production.

During the month of June, 1920, the casting plant melted 11,027,000 lb. (4,962,150 kg.) of cathodes, which was the production of the electrolytic division for the month. From this weight of cathodes, there was produced 9,709,000 lb. ingots, 788,000 lb. zinc dust, and 640,000 lb. dross. The ingots assayed as follows: zinc, 99.937 per cent.; cadmium,

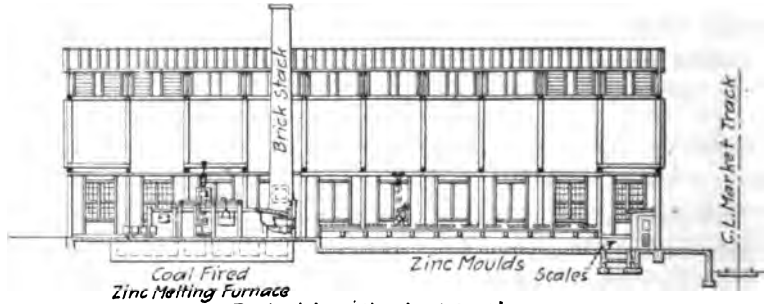
0.025 per cent.; lead, 0.035 per cent.; iron, 0.003 per cent. The dross contained 83 per cent. zinc.

Zinc-dust Plant

Approximately 8 per cent. of the zinc produced in the tank room is required to precipitate copper and cadmium. The zinc atomizing plant is made in two units, either may be shut down without interfering with the other. Each unit consists of an oil-fired Rockwell furnace, two blowing nozzles, and a settling chamber, with a superimposed bag house. The



Typical Cross Section



Typical Longitudinal Section

Fig. 18.—Casting division.

Rockwell furnace receives the molten zinc from the melting furnace by means of an electric hoist ladle and crawl system. The carbon crucible of the Rockwell furnace is provided with two carbon rods in the bottom, tapped with ⅛-in. (3.2 mm.) holes through which the molten zinc flows to the atomizing nozzles. Air from the nozzles strikes the hot zinc at right angles and blows it into the settling chamber. This chamber has bags above through which the air is filtered, leaving the dust to drop back into the hoppers which are provided in the bottom of the chamber to draw the dust into cars. One man per shift operates the plant.

There are three factors to be considered: (1) The metal must be hot. (2) The air pressure should be at least 85 lb. (38.5 kg.) at the nozzle. (3) The stream of metal should be small, not over 3/16 in. (4.7 mm.) in diameter. If the air pressure at the nozzle is 300 lb., less attention must be paid to the other two factors.

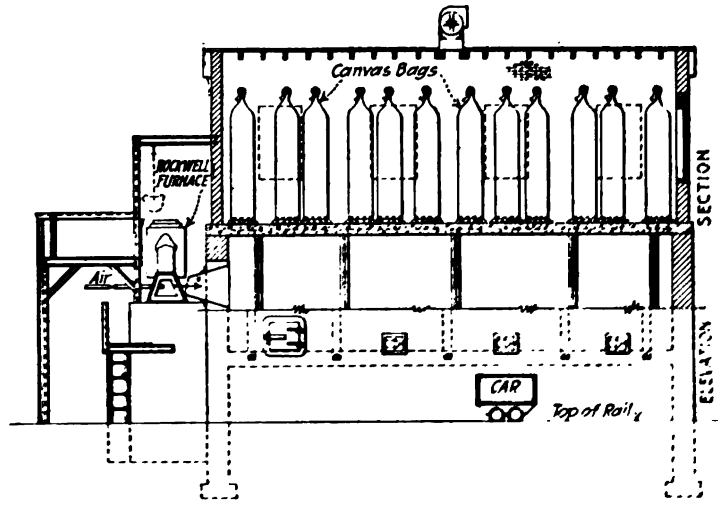


FIG. 19.—ZINC-DUST PLANT.

RESIDUE TREATMENT

Dryers

The wet residue from the Oliver filters is delivered by conveyor belt to the residue dryer plant. This plant contains two 7 by 50-ft. (2 by 15-m.) Ruggles-Coles dryers and three 9 by 60-ft. (2.7 by 18-m.) horizontal, single tube, rotary dryers. These dryers are coal fired and are fed by a belt conveyor. They are equipped with suction fans to provide draft and to discharge the gases to a double-compartment settling chamber and thence to the dryer stack. In passing through the dryers, the residue is reduced from 25 to 7 per cent. moisture and is then conveyed, by drag line, to an elevator which discharges into a concrete temporary storage bin. The residue from this bin is taken in 50-ton, standard-gage, railway, steel dump cars to the mixing plant.

Mixing Plant

The mixing plant consists of a bin containing eight 500-ton compartments. The first three compartments are used for fired residue, the fourth for fine coal, the fifth for siliceous ore, the sixth for upper con-

centrates, the seventh for lime rock, and the eighth for circulating material such as converter slag and cleanings. Each compartment discharges through a small measuring chute of known capacity on to a belt conveyor, which discharges into a storage bin.

Each day the charge is calculated by the smelting superintendent, who gives the head mixer the number of chutes of each ingredient to be pulled to form the charge. The head mixer, with two helpers, mixes from 500 to 600 tons of charge for the two reverberatories. A charge consists of approximately 4 tons of material, made up as follows: residue, 13 chutes; fine coal, 1½ chutes; siliceous ore, 1½ chutes; copper concentrates, 1 chute; fine limestone, 3½ chutes.

FIG. 20.—FINISHED SLAB WEIGHING 50 LB.; 99.90 TO 99.95 PER CENT. ZINC, 0.02 TO 0.05 PER CENT. LEAD, 0.01 TO 0.05 PER CENT. CADMIUM, TRACE OF IRON. COMPOSITION DEPENDENT ON DEGREE OF SOLUTION PURIFICATION.

These ingredients, as far as possible, are run on the traveling conveyor belt at the same time so that the mix will be uniform. However, in case each ingredient is run on separately, it is mixed by the spill into the bin and the handling it gets between the end of the belt and the furnace. The mixed charge is taken in 18-ton, standard-gage cars to the reverberatory furnace charge hoppers from which it is fed nearly continuously into the furnace.

Reverberatory Furnace

The reverberatory furnace is 125 ft. long by 22 ft. wide by 8 ft. high (38 by 6.7 by 2.4 m.) on the inside, measured from the silica bottom to the bottom of the arch about the center of the furnace. There are two of these furnaces, which were originally built to smelt copper calcines and were remodeled by lowering the bottom 2 ft. (0.6 m.), to increase the cross-section, and by increasing the size of the flue connection to the boiler, so as to permit as much settlement of the lead fume as possible. The flue is 6 by 8 ft. and would be better if it were larger and had hoppers for cleanout instead of side doors. The settled fume, or reverberatory ash, is rabbled out through these side doors and shipped to the lead smelter at Tooele for treatment. The slag is skimmed twice a shift into 15-ton slag pots and taken to the storage dump. It is planned to retreat this slag, at some future date, for the recovery of its zinc content. The matte is tapped into 15-ton matte ladles and charged into a 12-ft. Great Falls converter.

Converter

After charging the matte into the converter, it is over blown before adding the siliceous flux so as to expel as much of the lead as possible. The converter slag is poured back into the furnace and the blister copper containing the gold and silver is cast into anodes for the copper refinery. The lead fumes from the converter are collected by means of a hood and flue system, which is connected to the bag house.

Flue System of Bag House

The fume-laden gases are conducted through the 8 by 10-ft. (2.4 by 3-m.) flue to four Sterling waste-heat boilers arranged in parallel. By

FIG. 21.—BAG HOUSE, SHOWING BALLOON FLUE AND LOADING SHED.

means of a damper system, either boilers one and two or boilers three and four may be cut out for cleaning, which must be done at least every 60 days. From the boilers the gases travel through a [illegible] ft. steel flue for 1200 ft. to the cooler pipes and bag house. The flue system is provided with hoppers and track for the removal of dust.

Cooling Pipes

There are [illegible] cooling pipes [illegible] in diameter by [illegible] ft. long arranged in parallel. Each pipe is in the shape of an inverted [illegible] and is equipped with a butterfly damper for velocity control. Whenever cooling by radiation is not sufficient to cool the gases to [illegible] cold air is drawn in through special doors between the cooler pipes and fans.

Fans

There are three large fans [illegible] of which are necessary to provide the draft for the furnace and the pressure in the bags. There are two American blower fans of [illegible] per minute capacity [illegible]

each and one of 350,000 cu. ft. per minute capacity when operating against a combined draft and pressure of 6 in. of water. The pressure on the bags is approximately 1 in. (2.5 cm.) although at times when some of the sections are cut out for shaking the pressure goes up to 1½ in. The smaller fans are belt driven from 300-hp. motors and the larger one is rope driven from a 600-hp. motor. Care must be taken to keep the fan vanes free from an accumulation of fume, which has a tendency to build up and throw the rotor out of balance.

Bag House

The bag house originally contained eleven sections of 138 bags, each 18 in. by 30 ft. (45 cm. by 9 m.); it is so arranged that any section can be cut out for shaking or repairs. The building is of brick and steel with

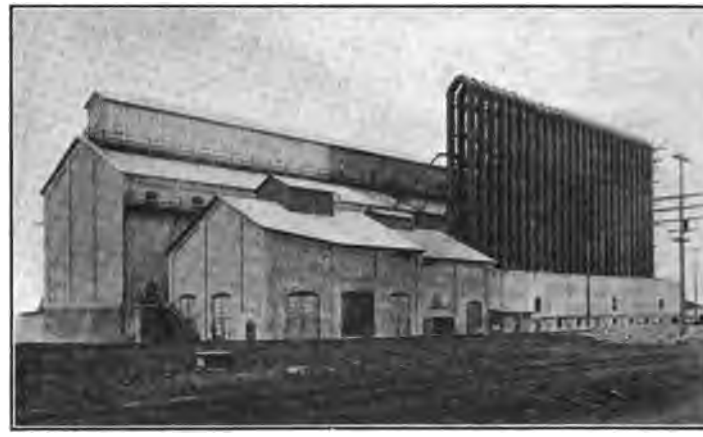


FIG. 22.—BAG HOUSE, SHOWING COOLER PIPES, FAN ROOM AND DISCHARGE FLUE OVER ROOF OF BAG HOUSE.

wooden sheeting and composition roofing. At first the gases, after being filtered through the bags, were allowed to diffuse into the air from louvers in the top of the bag house; the small amount of sulfur dioxide, 0.5 per cent. by volume, however, made working conditions very disagreeable. The bag-house openings were therefore connected to the main flue system, which discharges all the smelter gases at an elevation of 500 ft. (152 m.) above the surrounding country. In 1918, six sections were added to provide additional capacity so that the matte could be converted at Great Falls. Owing to the scarcity of steel, the roof trusses of these sections were made of wood, but it is now necessary to replace them with steel. The temperature has never been above 100° C., yet the wood ears to be changed to charcoal to a depth of ½ in. There is a cross nection between the suction flue to the coolers and the distributor flue

to the sections so that when the dampers are opened in the cross flue, a back draft results and the bags are collapsed and the exhaust gas from the section is forced into the bags of the other sections. In addition to collapsing, the bags must be hand shaken at intervals to remove the dust, otherwise the pores will be gradually filled. The bag dust falls into a special hopper under each section. A screw conveyor removes this dust to a cross conveyor, which discharges it into standard-gage railway cars for shipment to the lead smelters.

Residue Smelting

The object of the residue treatment is to collect the maximum amount of copper, gold, and silver in a leady matte with a minimum amount of zinc and to slag as much of the zinc as possible, while making a fume rich enough in lead to ship as a lead product. After several months of experimental work, the slag decided on as the most economical was 29 to 30 per cent. FeO, 27 to 28 per cent. silica, 16 to 17 per cent. lime, and 10 to 11 per cent. zinc. Over a period of six months when smelting a residue of the approximate analysis 15 per cent. lead, 13 per cent. zinc, 2 per cent. copper, 23 oz. silver and 0.07 oz. of gold, 12 per cent. silica, 29 per cent. iron oxide, the recoveries were: copper, 90.78 per cent.; gold, 74.05 per cent.; silver, 93.04 per cent.; lead, 72.65 per cent.

Miscellaneous Data

Fig. 23 gives an average set of operating data obtained in roasting low-grade complex concentrate from the Butte district. All flue dust produced by the roasting plant is returned to the furnace roasting this material, which accounts for the presence of soluble zinc in the feed. The samples for these curves were taken as indicated by the numerals on the diagram of Wedge roaster, Fig. 23. About 75 per cent. of the total sulfur is eliminated by the time the concentrate reaches the fourth roasting hearth and it is beyond this point that the formation of sulfates begins. The curves also show the increase in zinc content up to the point where elimination of sulfide sulfur is slow and the formation of sulfates is rapid, giving an increase in weight of calcine from addition of oxygen necessary to form sulfates.

It is not advisable to attempt to reduce sulfide sulfur in low-grade calcine below 0.5 per cent., as the formation of ferrate increases rapidly with the necessary increase in temperature or length of time. The consumption of fuel also increases out of proportion to the benefits derived from complete elimination of sulfide sulfur.

The production of flue dust from the roasting of low-grade concentrates is higher than from the roasting of high-grade concentrates due to

admission of a greater volume of air for cooling on the upper hearths. The higher percentage of iron sulfide in the low-grade concentrates accounts for the greater percentage reduction in sulfur on the upper hearths to obtain any desired percentage of soluble zinc. To obtain a product containing 40 per cent. of the total zinc in soluble form requires the elimination of approximately 35 per cent. of the total sulfur in high-grade concentrate, as against approximately 55 per cent. of the total sulfur in the low-grade concentrate. Roasting of iron sulfide is carried on at a lower temperature than the roasting of zinc sulfide and the effort is

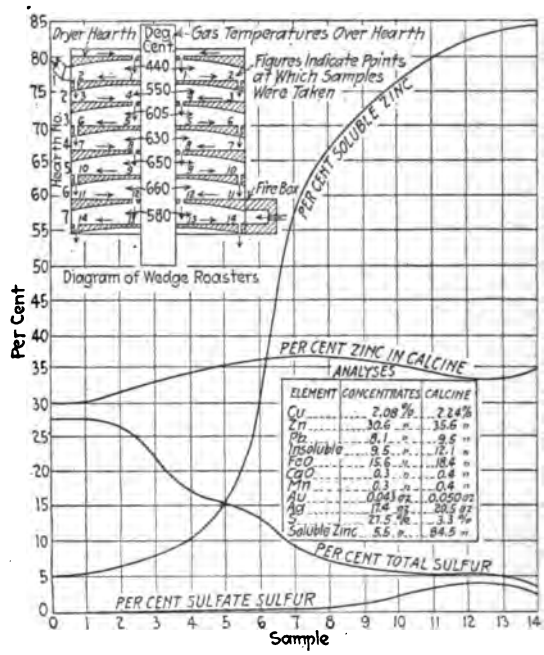


FIG. 23.—ROASTING LOW-GRADE CONCENTRATES IN WEDGE FURNACE.

made to roast the bulk of the iron sulfide before starting the roast of zinc sulfide. By so doing, the percentage of zinc ferrate is materially reduced and less trouble is had with hearth accretions.

Fig. 24 shows the reactions taking place in the roasting of a low-grade, complex concentrate. The samples of material passing through the furnace were taken at points designated to show the effect of passing across the hearths and in dropping from one hearth to the next. The concentrate used was a flotation concentrate, giving greater changes in dropping from one hearth to the next than would be the case with coarser material.

The proportion of sulfur burned off on the upper hearths to the amount of soluble zinc formed is different to that on the lower hearths due to roasting sulfides of iron on the upper hearths with as little zinc sulfide

being roasted as is possible with ordinary temperature control. Roasting of zinc sulfide begins as the material falls on to the third roasting hearth and after 25 per cent. of the total sulfur has been eliminated. Practically no sulfates are formed until the fourth hearth is reached and 75 per cent. of the total sulfur has been eliminated. The conversion of sulfide sulfur to sulfates from this point on is rapid and accompanied by an increase in weight and decrease in percentage of zinc although the amount of soluble zinc increases until the seventh hearth is reached.

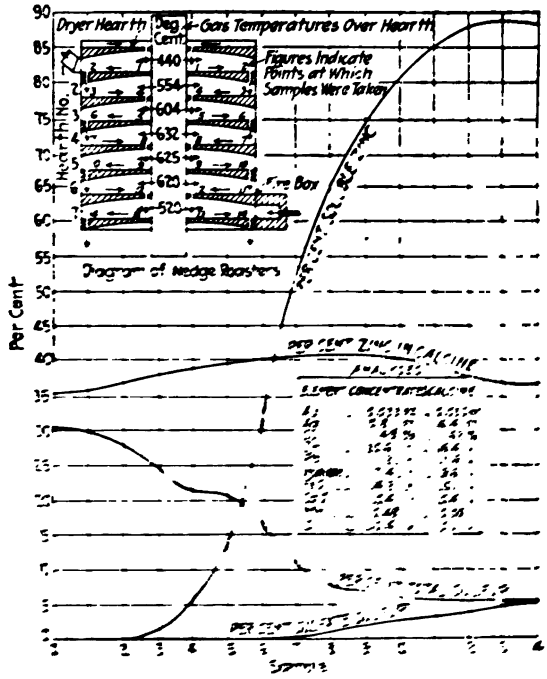


FIG. 24.—ROASTING LOW-GRADE CONCENTRATES IN WEDGE FURNACE WITHOUT RETURNING FLUE DUST

Fig. 25 gives an average set of data obtained in roasting high-grade zinc concentrates from the Butte district, without returning flue dust with the raw concentrate feed. This material is roasted separately from the low-grade material as a much higher temperature is required to eliminate the sulfide sulfur from high-grade than from low-grade concentrates. All flue dust produced goes to a common settling chamber and it is not desirable to return flue dust high in iron to the furnaces carrying a high temperature due to excessive ferrite formation at the higher temperature. All flue dust is therefore returned to the furnaces operating on low-grade concentrates.

The diagram of a furnace showing the location of points of sampling

illustrates the method of obtaining the samples from which the curves are plotted. The first sample was taken as concentrate dropped from the dryer hearth on to the first roaster hearth. The second was taken after the concentrate had passed across the first roaster hearth, just before it reached the drop hole to carry to the second roasting hearth. The third was taken after the concentrate had dropped from the first roasting hearth on to the second showing the roasting obtained in dropping from the first to the second roasting hearth. The fourth was taken after the concentrate had passed across the second roasting hearth and just prior to

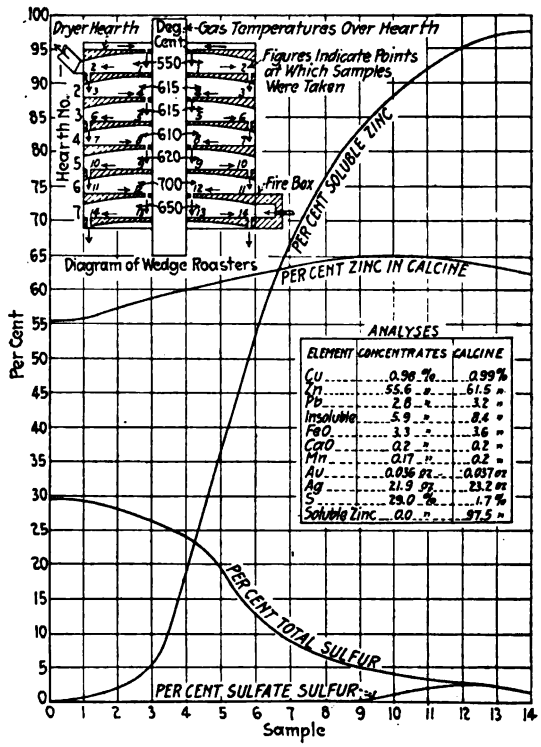


FIG. 25.—ROASTING HIGH-GRADE CONCENTRATES IN WEDGE FURNACE.

dropping on to the third roasting hearth. The other samples were taken in the same order until the fourteenth which represents the finished calcine.

Practically no sulfates are formed until the material reaches the fifth roasting hearth. At this point, most of the sulfide sulfur has been eliminated and the greatest loss in weight from concentrate to calcine is obtained, giving a product with the highest percentage of zinc but less than 85 per cent. of which is soluble, due to remaining zinc sulfide. As the percentage of sulfates increases, the per cent. of sulfide sulfur decreases but the material increases in weight, due to the oxygen taken up to form

sulfates, thereby decreasing the per cent. zinc in the calcine but increasing the amount of soluble zinc. If carried further at a temperature sufficiently high to break up the sulfates formed, the per cent. of zinc in the calcine will increase without increasing further the amount of soluble zinc. The per cent. of sulfur present as sulfates in roasting this grade of concentrate rarely reaches 3 per cent. and is usually between 1 and 2 per cent. when the sulfide sulfur is reduced to a few tenths of 1 per cent.

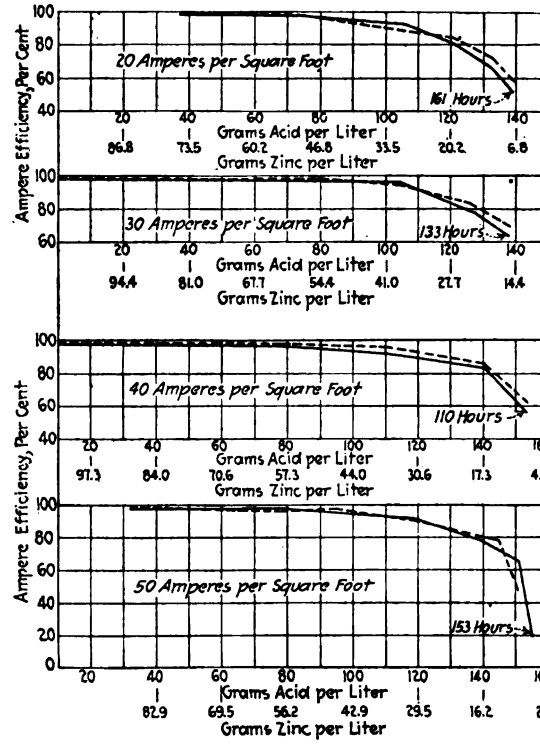


FIG. 26.—EFFECT OF TIME OF DEPOSITION AND RATIO OF ACID TO ZINC CONTENT OF ELECTROLYTE ON AMPERE EFFICIENCY. DOTTED LINE IS PLOTTED FROM 8-HR. DEPOSITS; SOLID LINE IS FOR CONTINUOUS DEPOSITION FOR HOURS INDICATED AT END OF LINE.

The sulfur elimination in dropping from one hearth to the next is nearly as great as in passing across the hearth, as is also the formation of sulfates. This is especially true in the roasting of fine material, such as the flotation concentrate used in obtaining the data plotted. The smaller the size of the particles, the greater is the surface exposed for a given weight and the greater the amount of sulfur burned in falling from one hearth to the next.

Fig. 26 is a summary of data obtained in a laboratory cell using a specially prepared zinc-sulfate solution. A large sample of zinc calcine

from the plant supply was leached in the laboratory with spent electrolyte from the large cells and sufficient potassium permanganate added to oxidize all iron present in the solution. An excess of calcine was added to neutralize all acid and precipitate iron, arsenic, antimony, alumina, and silica. The leach was filtered and the filtrate purified of copper and cadmium by means of zinc dust. This pulp was filtered and the solution used for the test cell runs recorded in these curves. The analysis of this solution was as follows:

	Grams per Liter		Grams per Liter
Zinc	110.0	Cadmium	0.002
Manganese	1.6	Iron	Trace
Copper	0.001	Sulfuric acid	0.0

Two cells were operated, making parallel runs. One cell was run at a continuous deposit for the full run, removing the cathode at 24-hr. intervals to weigh, in order to determine the ampere efficiency. The cathode deposit in the second cell was stripped at 8-hr. intervals and the ampere efficiency calculated; little difference, due to length of time of deposition, was noted. When impurities are present consistently higher ampere efficiencies are obtained with 24-hr. deposits than with 48-hr. deposits under identical conditions; it has been found impossible at times to operate the plant with 48-hr. stripping intervals, when fair deposits were obtained at 24-hr. intervals. This is additional proof of the care necessary in the preparation of solution for electro-deposition of zinc.

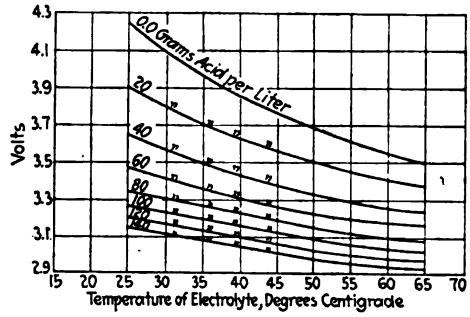


FIG. 27.—EFFECT OF TEMPERATURE ON RESISTANCE OF ELECTROLYTE AT 20 AMPERES PER SQUARE FOOT.

It has long been noticed that as the acid content of the electrolyte increases and the zinc content decreases, the ampere efficiency decreases. The decrease is gradual at first but after a certain point is very rapid. To determine this point for different current densities, a series of runs were made starting at 20 amp. per sq. ft. and ending at 50. In the 20-amp. run, some acid was added at the start of the run to prevent sprouting; smaller amounts were added to the succeeding runs. The current density employed, within the limits of the test, apparently had little influence on the efficiency obtained. In all the tests, and with both continuous and 8-hr. deposits, when the ratio of acid to zinc in the electrolyte exceeded 2.5 : 1 there was a marked decrease in ampere efficiency. It is not intended to state that this ratio will cover electrolytes containing

higher or lower zinc contents than the one employed—100 to 110 gm. of zinc per liter. In general, with pure solutions a long period of deposition may be employed without impaired ampere efficiency provided that the ratio of acid to zinc in the electrolyte is kept below a definite point.

When impure solutions are employed, the period of deposition must be shortened and the ratio of acid to zinc content of electrolyte must be lowered well under the critical ratio to obtain even average ampere efficiency. A fair deposit will build for a period, depending on the amount of impurity present, and will then redissolve to a point where the ampere efficiency drops to zero and the zinc deposited will partly or completely redissolve.

Figs. 27 and 28 show the variation, at constant acidity, in resistance of electrolyte at different temperatures. The variation is less marked with high acid percentages than with low acid percentages. At 20 amp. per sq. ft. and no acid, an increase of 40° C. reduces the required voltage by nearly 0.8 volt, or 0.02 volt per 1° C. With the same current density and 100 gm. acid per liter, the decrease in voltage is only 0.2 volt, or 0.005 volt per 1° C. With increased current density the change becomes more pronounced. At 50 amp. per sq. ft. and 100 gm. acid per liter, the change is 0.35 volt in 40° C., or nearly 0.01 volt per 1° C. With neutral solution, the decrease in voltage amounts to 2.8 volts for 40° C. increase in temperature, or 0.07 volt per 1° C. In general, the relation may be expressed by saying that the decrease in voltage due to increasing the temperature of an electrolyte is greater the higher the current density and the lower the acid content, the effect becoming less pronounced as the temperature increases.

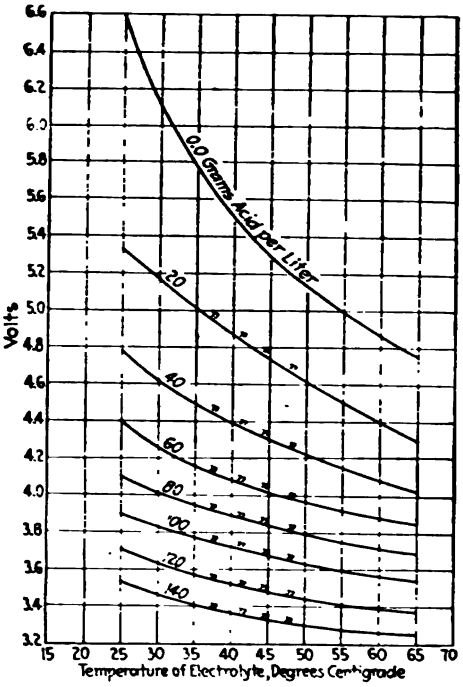


FIG. 28.—EFFECT OF TEMPERATURE ON RESISTANCE OF ELECTROLYTE AT 50 AMPERES PER SQUARE FOOT.

Fig. 29 shows the effect of increasing the temperature of zinc-sulfate solutions on the voltage required at various current densities and ratios of acid to zinc content of electrolyte. With pure solutions, an increase in temperature is not objectionable as affecting ampere efficiency. With

impure solutions, the effect of the impurities is magnified by increasing temperature and acid to zinc ratio of electrolyte. As the purity of electrolytes is better than it was several years ago, it is reasonable to assume that methods of purification will be perfected to insure still purer solutions, and increased temperature in the cells will be permissible. These curves indicate the saving in power that can be made to justify the expense of further purification.

The data for the first set of curves were obtained in a laboratory cell equipped with a cooling coil to hold the temperature constant at 25° C.,

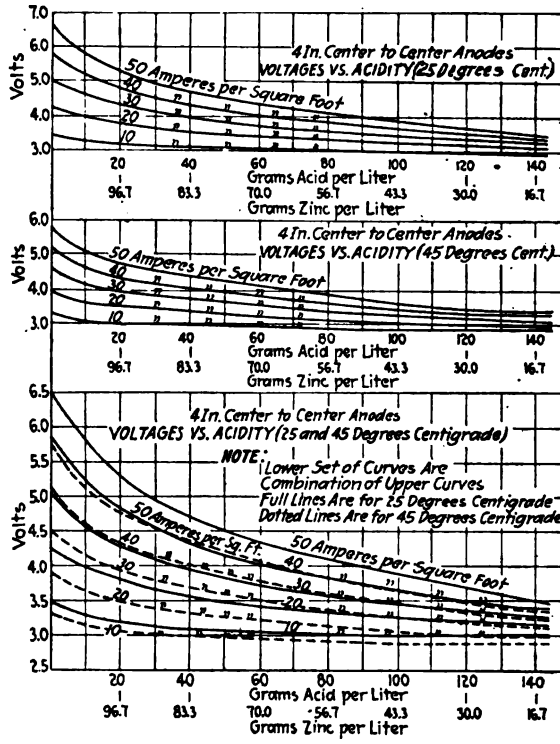


FIG. 29.—EFFECT OF TEMPERATURE AND ACIDITY ON RESISTANCE OF ELECTROLYTE FOR VARYING CURRENT DENSITIES.

which is as low as it is usually possible to hold the temperature of cells under operating conditions. The data for the second set were obtained in the same cell using steam coils to hold the temperature at 45° C. The third set is a combination of the first two and shows the comparison between the data obtained at 25° C. and 45° C. The broken lines are 45° C. readings and the solid lines 25° C.

The power consumed, assuming equal ampere efficiencies, at 50 amp. per sq. ft. at 45° C. with 14 per cent. acid in the electrolyte equals that

for 30 amp. per sq. ft. at 25° C. with 12 per cent. acid in the electrolyte. When the problem of producing an electrolyte of absolute purity has been solved, the design of electrolytic zinc plants and the operating conditions of the electrolyzing division will be greatly changed from the present trend. Where 75 per cent. ampere efficiency is now considered good practice, 85 to 90 per cent. is easily obtainable with slightly more pure solutions and temperatures of 60° C. are not objectionable, current densities can be increased and the ratio of acid to zinc in the electrolyte can be carried consistently higher than at present, giving even better cathode deposits. The length of time of deposition can also be doubled without impaired efficiency. Pure solution is the greatest single factor in the successful production of electrolytic zinc.

Fig. 30 shows a range of temperatures between 25° and 65° C. at 10° intervals for acidities varying from 0 to 13 per cent. As the tem-

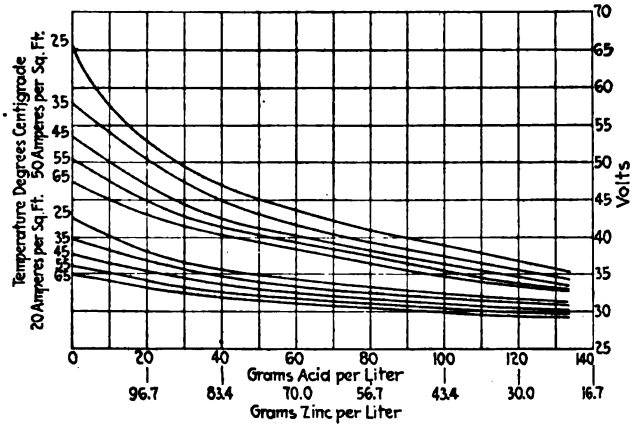


FIG. 30.—EFFECT OF TEMPERATURE AND ACIDITY ON RESISTANCE OF ELECTROLYTE AT 50 AMP. AND 20 AMP. PER SQ. FT. OF 4-IN. SPACING CENTER TO CENTER ANODES.

perature increases, the decrease in resistance due to increase in acid to zinc ratio becomes less. It is nearly as economical, assuming equal ampere efficiency, to operate at 50 amp. per sq. ft. and 65° C., with 13 per cent. acid as to use 20 amp. per sq. ft. at 25° C. with 13 per cent. acid. As the acidity decreases, the power consumption is increasingly lower in favor of the low current density, at either the lower or the higher temperature. An increase in either temperature or acidity brings the voltages required for different current densities closer together; therefore, if a sufficiently pure solution can be obtained to permit the use of high temperature and acidity without lowering ampere efficiency, the current density employed can be greatly increased over that for low temperature and acidity, without increasing power consumption.

Fig. 31 shows the power required under varying operating conditions

as regards current density and acidity of electrolyte, with spacing of electrodes and temperature of electrolyte remaining constant. Power efficiency is the percentage of the theoretical, taking the theoretical decomposition voltage of zinc sulfate at 2.35 volts and using 100 per cent. ampere efficiency. The points for these curves were then determined

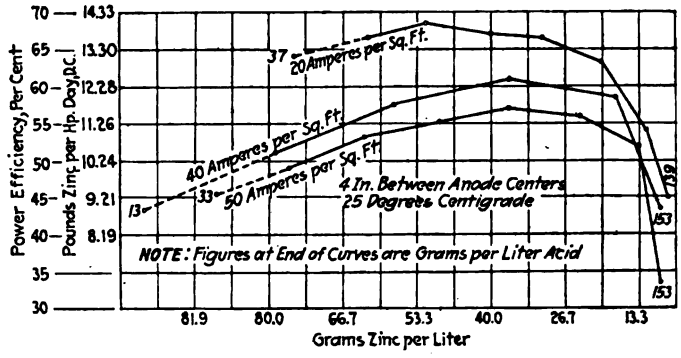


FIG. 31.—RELATION OF POWER EFFICIENCY TO VARIATIONS IN CURRENT DENSITY, ACIDITY, AND AMPERE EFFICIENCY.

from experimental work in which complete data were obtained for voltage and ampere efficiency variations with variations in the acid to zinc ratio of electrolyte. Although the voltage required decreases steadily with the increase in acidity, the ampere efficiency falls rapidly after the acid to zinc ratio increases above a certain point and the power efficiency also

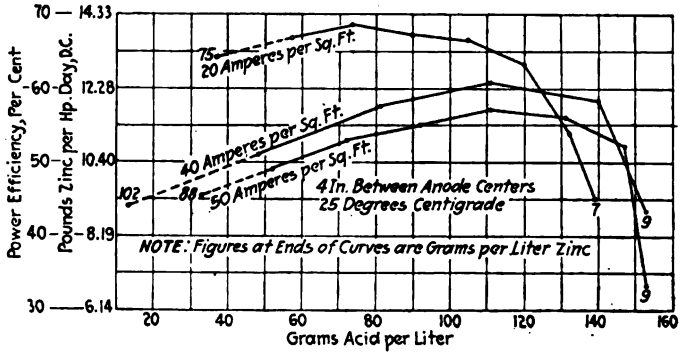


FIG. 32.—RELATION OF POWER EFFICIENCY TO VARIATIONS IN CURRENT DENSITY, ZINC CONTENT, AND AMPERE EFFICIENCY.

falls as the drop in ampere efficiency is too rapid to be made up by the decrease in voltage from increased acidity. At this temperature (25° C.) and with the acid to zinc ratio at higher acidities as shown, the higher current densities cannot compete with the lower except in cases of extremely cheap power.

Fig. 33 gives the power efficiency when the acid to zinc ratio is kept above the critical point. Provided that sufficient zinc were in the electrolyte to maintain a safe ratio and the acid content was further increased, the curves would apparently continue to flatten out until the power

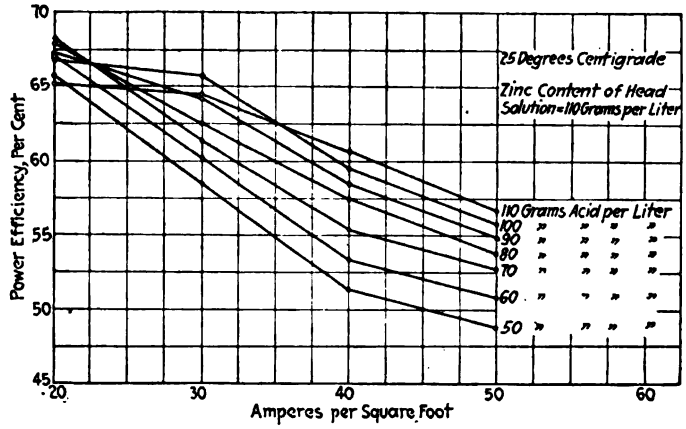


FIG. 33.—POWER EFFICIENCY FOR VARYING CURRENT DENSITIES AND ACID TO ZINC RATIOS.

efficiency for 50 amp. per sq. ft. equaled or exceeded that for the lower densities. Increased temperature would hasten this equalization as shown in earlier curves. The curves relating to power efficiency are not intended to be conclusive or final but point the way for additional research work. It will require considerable work to cover all phases of the varying influences and the practical application of electrolytic zinc is too recent for more than mere references to these important points.

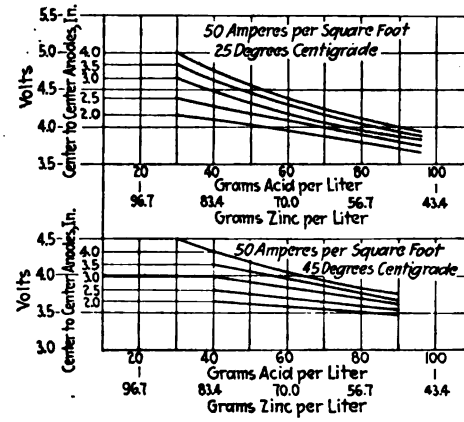


FIG. 34.—RELATION OF SPACING OF ELECTRODES TO VOLTAGES REQUIRED.

Fig. 34 was plotted from data obtained in a laboratory cell. At 25° C. and 2 per cent. acid, 2-in. (5-cm.) spacing of anodes requires nearly 1 volt per cell less than 4-in. spacing of anodes. At the same temperature and 10 per cent. acid, the difference is only ¼ volt. At 45° C. and 10 per cent. acid, the 4-in. spacing requires nearly exactly the same voltage as 2-in. spacing at the same acidity of electrolyte and 25° C. The losses due to short circuits and other operat-

ing troubles preclude the use of 2-in. spacing of anodes at the present stage of development of the process. If it is possible to effect a saving of 0.1 volt per cell by ½ in. closer spacing of anodes, there will be a saving of nearly 3 per cent. of the power bill in plants having an average voltage drop of 3.5 volts per cell. The average acid content of electrolyte in plants is not over 8 per cent. and at this point, either at 25° or 45° C., the saving is about 0.2 volt per inch reduction in spacing of anodes.

Fig. 35 is made up from data obtained under actual operating conditions. The current density was varied by removing cathodes from the cell from which the voltage readings were obtained, using different cells

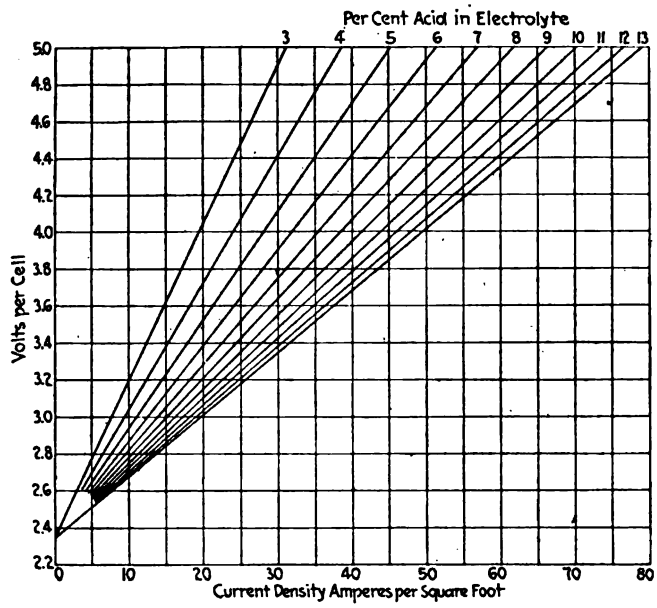


FIG. 35.—VOLTS PER CELL FOR DIFFERENT CURRENT DENSITIES AND ACIDITIES FOR 2-IN. SPACING OF ELECTRODES AT 35° C.

for each acidity. The distance from center of anode to center of cathode was 2 in. using ⅜-in., anodes and ⅛-in. cathodes. The neutral solution contained slightly over 100 gm. zinc per liter. The decomposition voltage of zinc sulfate (2.35 volts) was taken as the voltage at zero ampere per square foot. All current densities are figured in amperes per square foot of active cathode surface.

Fig. 36 shows data taken from operating records and is intended to show the effect of decreasing the resistance of electrolyte by increasing acidity. The head solution, or cell feed, contained slightly over 100 gm. zinc per liter, leaving only about 20 gm. zinc per liter in the tail solution, or cell effluent.

The yearly cost for power alone for the deposition of 100 tons of zinc per day for one year is given using a rate of $33.50 per kilowatt-year for power and 80 per cent. ampere efficiency. This does not include substation expense, upkeep of equipment, or any expense whatever but the payment for power at the transformer; conversion losses are included. Increasing acid content of cell effluent from 5.8 to 10 per cent. effects a saving of $42,600 per year for a plant producing 100 tons of zinc per day, or nearly $10,000 for each 1 per cent. increase in acidity.

The power consumption per ton of cathode zinc produced is also given as an aid in estimating the power consumption to be expected under any similar conditions. The curve will not hold good for the high acids when the zinc content drops below about 30 gm. per liter, at this current density, because of falling off in ampere efficiency. The voltage

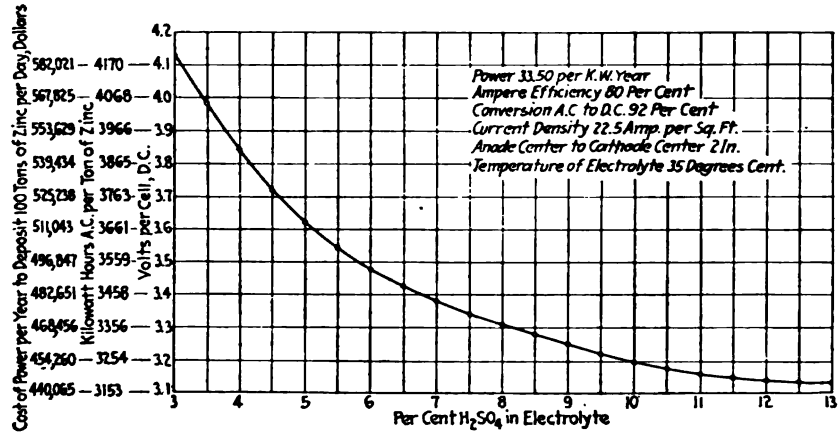


FIG. 36.—EFFECT OF VARIATION OF ACIDITY ON POWER COST AT CONSTANT CURRENT DENSITY.

readings will remain but the power consumption per ton of zinc will rapidly increase due to the decrease in ampere efficiency.

Fig. 37 gives the percentage distribution of the total power required to operate both zinc plant and residue treatment plant, together with the auxiliary departments, such as coal pulverizer and crushing plant. The bulk of the power is consumed by the electrolyzing division, therefore the base is taken at 75 per cent., which is below the minimum percentage consumed by that department.

Direct current to cells increases, roughly, in direct proportion to the quantity of zinc produced regardless of grade of concentrate treated; therefore, as the production of zinc increases the proportion of total power consumed by the cells increases. Increased production is usually obtained by raising the grade of concentrates treated, thereby increasing the production of zinc without proportionately increasing the equip-

ment in operation, other than cell equipment. Ampere efficiency, resistance of electrolyte, current density, and temperature of electrolyte influence the amount of power consumed by the cells, but taken over a long period it will not be far from proportional to the zinc produced.

Conversion losses include all losses from alternating-current transformers to the direct-current switchboard. A converter carrying full load, but not an overload, has a lower conversion loss than an underloaded converter. The normal loss of power from alternating to direct current is about 8 per cent.

Zinc roaster power is in proportion to the number of furnaces operating and the tons feed. The power consumed by the Anaconda roasters is

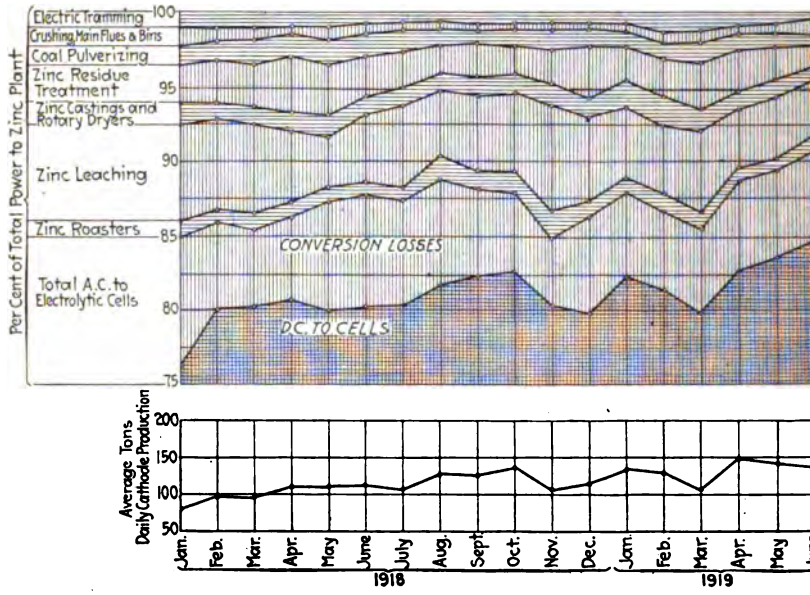


FIG. 37.—DISTRIBUTION OF POWER TO ELECTROLYTIC ZINC PLANT.

not included in this chart, therefore the data prior to 1919 are more accurate for this department.

Zinc leaching power is largely dependent on tonnage of material handled, as the greatest power consumption is for supplying compressed air and in the filter division. The consumption of air is dependent more on the volume of solution handled than on the tonnage of solids, but with a constant grade of calcine and zinc content of solution, the amount of solution handled is roughly proportional to the tonnage of solids.

Zinc residue treatment power varies with the method of disposal of residue and the quantity being treated at Great Falls. The frequent changes in method of disposal and in the equipment used are responsible for the frequent variations shown.

The other departments are small users of power and the variations are mainly dependent on the tonnage treated.

ACKNOWLEDGMENTS

The authors here take the opportunity to acknowledge the many helpful suggestions received during the development of the process, and wish to state that the visits of persons interested in the development of electrolytic zinc were both helpful and inspiring; much of the progress can be traced to this interchange of ideas. Our visits to other electrolytic zinc plants were no less helpful.

We also wish to acknowledge our indebtedness to the junior members of the staff, who by their untiring effort and loyalty made the plan a success. Also to the construction and mechanical departments, as the process was being developed at the same time as the plant was being designed and constructed and as it was often necessary to rebuild old equipment because it was impossible to obtain new.

DISCUSSION

STANLEY C. BULLOCK, London, Eng. (written discussion).—There seems to be no radical difference from standard practice in the method adopted by the operators to obtain a product suitably calcined for leaching, but the paper does not make clear what is the usual percentage of total zinc made soluble by roasting under conditions usually employed in their operating plant. In England, where only hand-rabbled furnaces of the Delplace type have been used for roasting, up to 97 per cent. of the total zinc in the concentrate has been made soluble, any figure below 90 per cent. is poor practice. Even Australian concentrates have given this solubility, and they require a more careful roast than the usual class of ore treated.

Several plants in America, in addition to that at Anaconda, appear to follow the double leaching method; *i.e.* first a neutral and then an acid leach. The most successful method in England is to leach with a hot solution, reducing the acid by the addition of the roasted ore or concentrate to 0.5 per cent. and completing the neutralization with calcium carbonate or the zinc hydrate precipitate from the deironizing process, which is carried out subsequently. The solution or pulp is then rendered alkaline by the addition of $CaCO_3$, to insure easy filtration and the absence of gels.

Deironizing is always carried out subsequent to filtration in the English process by simple aeration methods combined with the addition of calcium carbonate to the hot solution. The precipitate formed is subsequently used during the leaching process for neutralization. Owing

to the large number of deleterious impurities in the British, Australian, and Indian ores, a more elaborate method of purification than that adopted at Anaconda has been found necessary on English plants.

After the iron, antimony, arsenic, etc. have been precipitated, it is almost invariably necessary to purify for nickel and cobalt, etc. as well as for the more easily eliminated impurities, such as copper, cadmium, etc. Copper, nickel, and cadmium are first eliminated by agitation and precipitation by zinc dust from the hot slightly acid solutions and filtered. This filtrate is then agitated, heated, and the necessary oxidizing reagent added for the cobalt precipitation. After filtration, the solution is taken to the mixing tanks, where it is brought up to the desired acidity, usually about 3 per cent. acid and 8 per cent. zinc, by the addition of electrolyte from the cells and is then ready for the tank house. The quantity of nickel and cobalt remaining in the solution must not exceed 0.0001 per cent. (1 part per million) and 0.001 per cent. (10 parts per million), respectively, though in actual practice they are seldom more than 0.00002 per cent. for nickel and 0.0005 per cent. for cobalt, by reason of the effective methods adopted for purification.

The elimination of these impurities has so simplified and increased the efficiency of the electrolytic deposition department that the small extra cost of the method is more than compensated for by the decreased power consumption and the high zinc contents of the pure solution flowing into the cells coupled with the low zinc contents of the out-flowing solution.

Cell-house practice appears to be identical with that in England. The potential difference per cell is usually about 3½ volts while the current density varies from 25 to 30 amp. per sq. ft. of cathode, and the cathode sheets are changed about every 24 hr. Earthenware cells have been used with satisfactory results, the current efficiency being about 90 per cent.

The solution entering the cells carries about 8 per cent. zinc and 3 per cent. acid, while the outflowing electrolyte carries about 3 per cent. zinc and 10 to 11 per cent. acid.

No difficulty is experienced in separating the zinc sheets from the aluminum cathode and the zinc is subsequently melted in an oil-fired furnace and cast into plates or ingots.

There is little doubt but that in this country, if not in Europe, the furnace or distillation method of zinc production from blende is doomed. Efforts are being made in Scandinavia to produce zinc on a commercial scale by electrothermic methods but owing to the quantity of impure zinc oxide and dirty slags produced it is questionable whether this method can compete with the electrochemical process.

W. C. SMITH, Chrome, N. J.—The question of impurities in electrolyte has been emphasized by the Anaconda metallurgists. Mr. Tainton,

at Martinez, Calif., found that with a high current density and a high acid content, he can have as high as 30 mg. per li. of cobalt. The impurity that he fights is antimony; arsenic does not bother him quite as much; he has handled as high as 30 mg. of arsenic without losing current efficiency. The average current efficiency during the time that I was visiting the plant was 89 per cent. One pound of zinc required 1.77 kw.-hr. electrical energy delivered to the cells. The spacing of the electrodes is $1\frac{3}{16}$ in. from the face of the anode to the face of the cathode; the average voltage is about 4 volts per cell.

Mr. Tainton has developed a leaching process that differs from the Anaconda practice.

The roasted ore is separated by means of a magnetic separator into approximately two equal parts: a magnetic, or ferrate, and a non-magnetic, or oxide, portion. In the leaching operation, the spent cell solution, containing approximately 27 per cent. free sulfuric acid, is treated with the magnetic portion of the roasted ore until the free acid content has been reduced to 12 or 13 per cent. The balance of the free acid is then neutralized by the addition of the non-magnetic, or oxide, portion of the ore. A precipitant for gelatinous silica is added before the free acid is completely neutralized. The hot neutral pulp from the agitator is then passed through a Burt filter. The solution from the filter averages about 200 gm. per li. of zinc, and if allowed to get cold will crystallize to a semi-solid mass. The solution is purified by means of zinc dust, hot agitation, and filter pressing. The required amount of this strong solution is added to the cell solution to bring the zinc in the cell solution up to about 70 gm. per li. The cell solution is circulated through the cells until the zinc has dropped to about 30 gm. per li. A portion of the cell solution is drawn off and sent to the agitators, and the solution is replaced with a strong solution from the purification cycle.

The average extraction of zinc from a 39 per cent. ore was 87.6 per cent. during the time that I was making the test; that is, an ore which was composed of a mixture of Federal ore, Nabob ore and Federal slime. The average ore contained about 7 per cent. of lead and 10 oz. of silver; the residue ran approximately one-half the weight of the ore treated, and showed a little less than 10 per cent. zinc.

F. G. Breyer, Palmerton, Pa.—Is the 87 per cent. of the recovery on the weight of the electrodes or on the weight of the cast slabs, that is, commercial slabs?

W. C. Smith.—It is on the weight of cathode sheet produced; the cathodes were not melted but were sold as cathode zinc.

Extraction varies with the grade of ore. For instance, ore from Shasta County, Calif., which ran about 5 per cent. copper and 42 per

cent. zinc, gave a very good extraction; I think it averaged over 92 per cent. A number of carloads of the Silver Standard ore, from Nelson, B. C., were also successfully treated. This mixture of Nabob ore, Federal ore, and slime that was being worked at the time of my visit was the meanest proposition they had been up against, because the Federal slime was all dust.

This plant is operated by the Central Mining Co., of London, using the Tainton-Pring process, the original patents for which are prior to the Anaconda patents.

T. T. READ, Washington, D. C.—How does the purity of the cathode produced at the high current density compare with the Anaconda?

W. C. SMITH.—As nearly as I can judge, the purity is about the same. You must have a reasonably pure solution to get a good zinc deposit, but the last traces of impurity, which are difficult to get out, do not have to be removed when using the high current density and high acid solution.

I omitted to state that they use about 3 lb. of glue per ton of zinc produced. That seems to have a very beneficial action on the amount of mist or gas and acid mist given off by the cells. At no time was it necessary to wear a respirator. The glue is added periodically, in fact the amount of acid mist is an indication of the amount of glue in the solution; if this is noticeably strong, glue is added. Its effect can be seen at once. The large percentage of glue probably increases the possibility of running a foul solution.

A. A. HEIMROD, New York, N. Y.—How was the iron content eliminated from the solution?

W. C. SMITH.—Manganese ore added in the leaching operation, oxidized the iron to the ferric state; the neutralization precipitates the iron, and sweeps down most of the arsenic and the antimony and other troublesome metals to a large degree.

G. L. OSTGREN, New York, N. Y.—How many men are required to operate a plant of, say, about 100 tons?

W. C. SMITH.—I cannot answer that. The plant was an experimental one with a maximum production of about 6 tons per 24 hr., but it was producing about 2 tons while I was there.

F. G. BREYER.—Was the 87 per cent. recovery a day's run, or was that the recovery of 100 tons of ore that was run through the plant?

W. C. SMITH.—Roughly, that represents ten or twelve days operation, of approximately 5 to 6 tons of ore a day.

W. SEGUINE.—With 100 amp. per sq. ft., how is it possible to operate on that zinc at the temperature of 84° F.? Does not the temperature rise to an extraordinary degree?

W. C. SMITH.—Without a doubt one of the most expensive installations in the plant was the cooling system. The electrolyte must be cooled after each pass through the cells. That feature required more experimental work and more tearing down and rebuilding than any other part of the plant. A fairly simple and inexpensive cooling system has been developed.

HIRAM W. HIXON, New York, N. Y.—Is there any claim for novelty as regards the use of glue? The Anaconda copper refinery 25 years ago used glue to obtain a denser deposit of copper.

W. C. SMITH.—It was the natural thing to try. First the copper refinery used glue, then the lead refinery, it was the natural thing for the zinc refinery to try glue.

E. P. MATHEWSON, New York, N. Y.—The men at Anaconda were pioneers in commercializing electrolytic zinc. The later workers, who are operating at Martinez, have discovered that they can get along with a much smaller plant by using a much higher current density. That means that the first cost of the plant is much less than the first cost of the plant at Anaconda. They have overcome much of the trouble of the impurities and can use much more impure solutions than would be possible under the practice of the Anaconda people. It seems likely that the production of zinc by strictly furnace methods will soon be a thing of the past except where electric power is extremely costly or fuel very cheap.

E. L. JORGENSEN, New York, N. Y. (written discussion).—The advantage gained by using higher current densities, as worked out in Martinez, Calif., would be increase in ampere efficiency, because the reduced effect of impurities in the electrolyte permitted the use of impure solutions, and the size of the electrolytic tank house could be decreased. A careful study of this question in connection with the electrolysis of copper-sulfate solutions shows results that should apply in a general way to electrolysis of zinc.

With increased current density follows an increase in cell voltage and, consequently, an increase in power consumption. In the electrolysis of copper, the cost of the electrolytic tank house is generally less than one-half the cost of the power installation. As the electrolytic tank house is decreased in size the power plant is increased, so it does not necessarily follow that a great saving in capital expenditure is

effected. As the power consumption per pound of zinc produced is increased, thereby increasing the operating cost, and as the increased power consumption results in heating the solution, necessitating cooling and increase of flow to avoid excessive temperatures, a point will be found beyond which it does not pay to go. This point depends entirely on local conditions.

It would seem that in certain localities it would be better to guard against impurities in the electrolyte in the manner practiced by the Anaconda Copper Mining Co. than to resort to the use of extremely high current densities.

In the electrolysis of zinc any power required in excess of 0.736757 kw.-hr. per lb. is used for heating solutions. The practice at Great Falls shows a power efficiency of 44.6 to 50.5 per cent., and at Martinez of 41.6 per cent. If the electrolytic power is produced in a steam-power plant, which will show an over-all efficiency of only 15 per cent. or less, we have an over-all efficiency for electrolysis of 6 to 7 per cent. This may suggest opportunities in looking for another method for the recovery of zinc from hydrometallurgical solutions.

J. O. ELTON AND R. B. CAPLES (authors' reply to discussion).—The first experimental work done at Anaconda was at high density. The results were so good that it was decided to try out this method thoroughly, but after a thorough trial it was decided that high-density work was impractical. Mr. Mathewson was manager of the Anaconda plant at that time when the 10-ton plant was designed for operation at 30 amp. density per square foot. We believe we are safe in saying that every company making electrolytic zinc has at one time or another investigated and turned down high-density methods. There is a vast difference between a small plant that can be closed down and overhauled every time something goes wrong and a big plant that must run every hour at full capacity to fill contracts for war needs.

Mr. Mathewson stated that a much smaller plant is required through the use of high-current density and that therefore the first cost is much less than for a plant using low density. Based on the experience of an electrolytic-copper refining plant, this statement sounds reasonable to any one who has not had much experience with the electrolytic zinc process. There are many differences between electrolytic-copper refining and the production of electrolytic zinc, and the effect on the process of changes, such as variations in current density, present entirely different problems. A detailed comparison of first costs for zinc plants employing high density and low density is not nearly as unfavorable to the low-density plant as might at first appear. The difference in operating and maintenance costs will return a high rate of interest on the added investment required for the low-density plant. As no high-density plant for

the production of electrolytic zinc on a commercial basis has yet been built, there is no actual basis of comparison of the first cost of such a plant and a low-density plant. A comparison of costs at the present time is therefore really a comparison between what may be reasonably expected from the high-density plant, based on small-scale experimental data, and what has been proved to be true for a full sized, commercial low-density plant after several years of successful operation under trying conditions, as regards labor turnover, securing supplies, etc.

Roaster Division.—From data published regarding zinc recovery in a high-density plant, the same quantity of material must be roasted for either a high- or a low-density plant. Leaving out the cost of magnetic separators, separate bins for the magnetic and non-magnetic portions,

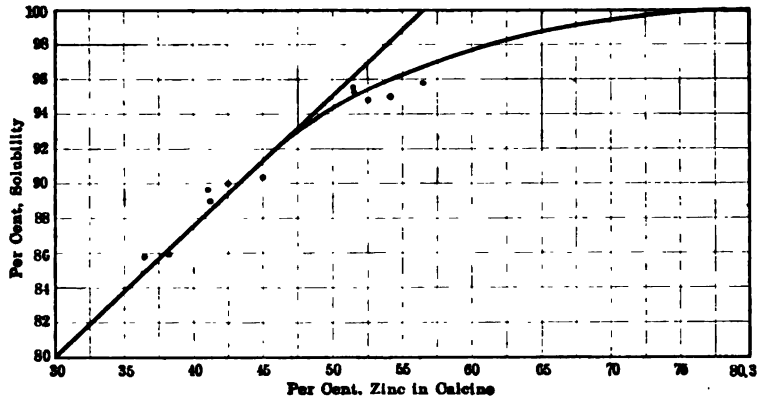


FIG. 38.

and other equipment necessary to conduct this step, the cost of the roaster division of each plant is the same. If magnetic separation of the calcine is used in the high-density plant, the cost of roasting equipment will be that much higher.

Leaching Division.—The floor space required for the low-density plant may be somewhat greater than for a high-density plant, due to the elimination of thickeners and handling less solution. More floor space for filters and solution storage is required in a high-density plant. The net difference will not amount to a large sum of money. A high-density plant requires lead-lined leaching tanks, mechanical agitators, and heating coils in all storage tanks. More material must be filtered under pressure and at high temperature and quantity and temperature of wash water must be carefully watched. A large boiler installation to supply steam for heating solutions is required. The cost of equipment in a high-density plant will equal, if not exceed, that necessary for a low-density leaching plant.

Electrolyzing Division.—Entirely different arrangements of cells are required for high- and low-density plants. In the former, one or possibly two cells are in series as regards solution flow; while in the low-density plant as many cells as required may be connected in series or cascade. It is necessary to return a large proportion of the spent electrolyte to be mixed with a small amount of new solution in order to keep down the voltage in a high-density plant, and this mixture is cooled before returning to the cells to keep down the temperature of the electrolyte. An elaborate system of lead pipes, pumps, cooling equipment and storage tanks is required to carry out these operations. In a low-density plant, it is unnecessary to return any acid solution to the cells, yet a practically uniform voltage drop per cell is maintained throughout the cascade, and the only cooling equipment necessary is a small lead coil in some of the cells in each cascade. The floor space required for a high-density plant is greater, in proportion to the number of cells, due to greater space taken up by aisles and working spaces, and a larger basement is required to accommodate the piping and pumps for circulating spent electrolyte. Using the same spacing of electrodes, at least 25 per cent. more power-generating equipment is required for a high-density than for a low-density plant. The total cost of electrolyzing division and power equipment is little, if any, in favor of the high-density plant, and the greater power cost so increases the operating cost that an enormous saving in first cost must be obtained to justify the high-density plant.

Casting Division.—The costs are the same in both cases.

Assuming all labor and supply costs to be equal and a difference of only 12½ per cent. in power consumption in favor of a low-density plant of 150 tons of zinc daily capacity, where power costs $30 per horsepower-year, there is a saving in power alone of over $112,000 per year, which will justify the expenditure in first cost of $1,000,000. There is no doubt but that the difference in first cost of the leaching and electrolyzing divisions for high-density and low-density plants of this size would be less than half this amount, and as the other divisions are practically equal in first cost it is now apparent how the first cost will justify the installation of a high-density plant. The total cost of the plants is not determined so much by the space covered as by the cost of the equipment covering it.

We emphasize the effect of impurities in the electrolytic process, stating that of all impurities encountered antimony is the most injurious. Mr. Gepp has had more trouble with cobalt. The effect of impurities is not eliminated by merely increasing the acidity of the electrolyte and increasing the current density. If the solution is cooled sufficiently (increasing power consumption and operating costs), or if the deposit is stripped at short intervals (increasing labor cost), or if proper addition agents are employed in sufficient quantity, the injurious effects of copper,

arsenic, antimony, and probably cobalt, are considerably lessened. But why resort to these measures instead of purifying the solution sufficiently in the leaching division? It is necessary, with unskilled labor, to make the process as nearly fool-proof as possible and at the same time to reduce the operating costs to a minimum. With an absolutely pure zinc-sulfate solution, anyone can successfully produce electrolytic zinc under nearly any cell condition desired. There is no great mystery or difficulty in eliminating arsenic or antimony from solution in the leaching division, and it is more economical than increasing power and other electrolyzing costs by allowing small amounts of these impurities to go to the electrolyzing division, necessitating cooling and "doping" of the electrolyte.

Mr. Smith states that the deposition of 1 lb. of zinc required 1.77 kw.-hr. under test conditions at the Martinez plant. We have produced zinc over a period of several months in the Great Falls plant under normal operating conditions with a consumption of approximately 1½ kw.-hr. per lb., with a spacing of 1 1/16 in. from face of anode to face of cathode against 1 3/16 in. at Martinez. With the closer spacing used at Martinez, the power consumed at Great Falls would be nearly 10 per cent. less, making power consumption at Martinez under test conditions 25 per cent. higher than at Great Falls under full-plant operating conditions. Mr. Smith gives the recovery of zinc from a 39-per cent. zinc ore as 87.6 per cent. With the Anaconda roasting practice and leaching system, this recovery can be duplicated on the same grade of ore if no deduction is made for loss of zinc in purification sludge from the complete removal of copper and cadmium solution, that is, from ore to gross cathodes. If sufficient zinc dust is added to completely remove all cadmium from solution (0.01 gm. cadmium per liter) a certain amount of the zinc recovered as cathodes is lost in the purification sludge. Mr. Smith does not give the cadmium content of the cathodes produced nor the amount of cadmium or copper in the ores treated.

The amount of mist given off from the cells is directly proportional to the action of impurities in the electrolyte; and with a pure solution little if any mist is given off, even without the addition of glue. The clarity of the atmosphere in the cell room is a good indication of the amount of resolution of the deposit in the cells. The mist is largely due to escaping hydrogen, and when only oxygen is being given off from the cells the gas bubbles are large and break quietly at the surface of the solution. The use of glue in the electrolysis of zinc-sulfate solutions at Anaconda dates back to 1915; varying amounts have been used up to the present time. We have continually striven to get away from it entirely by producing a pure solution. One objection to the use of glue is the amount of chlorine present, causing anode corrosion, but the chief objection is the desire to avoid using any solution dope.

Mr. Bullock's question as to the usual amount of zinc made soluble

in the Great Falls roasters can best be answered by referring to the last paragraph of page 706 and to Figs. 23, 24, and 25. The curves portray the regular practice, as the samples from which the data were obtained were taken from normally operating furnaces. It is not fair to compare solubilities obtained from the roasting of widely differing ores or concentrates; each concentrate is a problem within itself. The mere fact that each contains the same total per cent. of zinc does not mean that equal solubilities are possible. However, it is possible to predict the solubility within reasonable limits. In general, a 30-per-cent. roasted zinc concentrate from a complex ore should contain 80 per cent. of its zinc in soluble form, if properly roasted. The solubility should increase ¾ per cent. for each increase in grade of 1 per cent. up to 45 per cent. zinc. Above 45 per cent. the increase in solubility is not so fast. Correction must be made for the sulfide zinc left in the calcine, after which the balance of the zinc may be assumed as soluble, either as oxide or sulfate. Fig. 38 gives a graphic presentation of the empiric curves with the December, 1920, daily assays indicated. If the daily assays fall near the empiric curve, the roaster superintendent feels that his department is doing good work. Concentrates high in insoluble or low in iron sulfide will give better solubilities than indicated by this curve.

The leaching process originally developed and used in the pilot plants, and up to December, 1917, at Great Falls was the single leaching scheme described by Mr. Bullock. The operating costs per pound of zinc recovered at the zinc plant were lower with this process than they have been with the double leaching scheme, but the recovery was approximately 15 per cent. under the theoretical and the residues were bulky, high in zinc and moisture, and greatly increased in weight due to the large amount of calcium carbonate used, which came down as hydrous calcium sulfate. It was also necessary to add several tons of acid per day to make up for the amount neutralized and entrained as zinc-sulfate solution in the residue. When mining costs, residue smelting tolls, freight on ore and residues, and zinc plant costs were taken into consideration, the double leaching scheme showed a decided advantage when working with our ore. In cases where the residues are relatively small, as in high-grade concentrates (50 per cent. or higher), or when the residues contain no other metal values, it is doubtful whether it would pay to use the double leaching scheme, because it requires more labor and equipment and repair costs are undoubtedly higher, especially on the acid filtering equipment. Careful consideration must be given to each problem and no general rules can be laid down.

Mr. Bullock's comments on purification are sound and to the point. It surely pays to purify in a commercial plant. Our purification process costs less than $3 per ton of zinc produced, although copper is present to the extent of 6 per cent. of the total zinc, and so far has prevented the

building up of any known impurity in the system. The same solution has been used continuously since the plant was started in September, 1916. Evaporation losses and moisture losses have been made up by adding wash water to the filters. Practically all elements are present in the ores treated, at least traces of most of them have been reported. Nickel is found in Butte ore and cobalt in the Coeur d'Alene ores. Our success with electrolytic zinc is due to the fact that we early recognized the necessity for intensive purification and developed an inexpensive method of doing it. We are as proud of the fact that we keep our solutions clean as that we keep our operating plants clean. The small amount spent in purification is more than made up in the tank room saving in power alone.

If Mr. Bullock will try feeding neutral solution to each cell in his system, it will be unnecessary to return any acid and the cell voltage can be made uniform in every cell. No acid return system is necessary, and all feedpipes can be made of iron. The saving in power will be a large item. The flow is much easier to control and operating and repair costs are less.

Tooele Flue-type Cottrell Treater

By A. B. Young,* Tooele, Utah

(New York Meeting, February, 1921)

It is the object of this paper to describe a Cottrell treater that was placed in operation, in April, 1919, at the Tooele plant of the International Smelting Co., for the purpose of recovering solids from the gases from the McDougall roasting furnaces. Fundamentally, the treater is simply a flue containing rows of vertical plates, forming the grounded electrode, alternated with rows of small horizontal pipes, forming the negative electrode, with proper provision underneath for taking away collected dust. There are advantages in construction over the more cumbersome types, both the vertical-tube and the vertical-box, particularly in the elimination of heavy supporting columns and massive foundations, giving a much lower first cost. There are no right-angle turns to interfere with gas distribution; consequently there is greater efficiency, or, in other words, a greater volume of gas per minute can be effectively treated. Another advantage of the horizontal installation over the vertical is that the principle of the selective precipitation of the various components of the dust and fume as they pass along the electric field may be utilized. Since the treater has been placed in operation, the results have been quite satisfactory and, in many ways, particularly in regard to the volume of gas that may be treated, have greatly exceeded expectations.

Description

In the original design of the flue system, the flues from the roasters delivered their gases to a large brick dust chamber which discharged into another flue with stack connection, as shown in Fig. 1. The treater is so situated that the gases are taken by it directly from the chamber and discharged again into the flue. The complete installation comprises two treater units, only one of which has been installed at present.

The treater is essentially a flue 10 ft. high, 12 ft. wide, and 61 ft. long. (3 by 3.6 by 18.5 m.). Suspended inside, vertically and running lengthwise, are four banks of No. 20 corrugated iron plates; each bank is 10 ft. long, making an effective treater length of 40 ft. The spacing from center to center of the rows of plates is 9⅛ in. (23 cm.) giving six-

*Superintendent, Tooele Plant, International Smelting Co.

teen rows of plates to a bank. Midway between the rows is a row of horizontal ¼-in. (6.35-mm.) pipes, running longitudinally; the vertical spacing between them is 6 in. The plates form the grounded and the

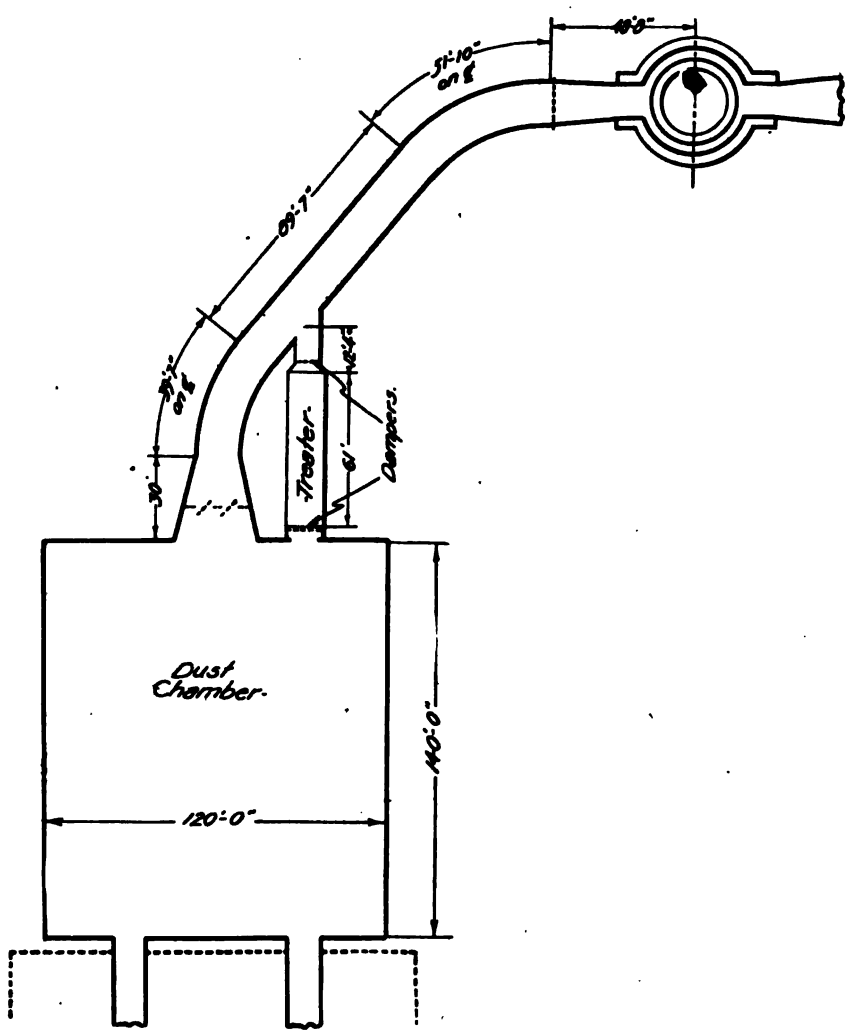


FIG. 1.—PLAN OF FLUE SYSTEM, SHOWING LOCATION OF TREATER.

pipes the negative electrodes. Allowing for the thickness of the plates and the area of the pipe sections, the treater has an effective cross-section of 113.5 sq. ft. (10.4 sq. m.)

Steel hoppers that discharge into a screw conveyor catch the dust underneath; the conveyor delivers into a small bin located in a shaft

beneath the treater. The bin may be emptied into reverberatory furnace charge cars upon tracks that run in a tunnel under the large dust chamber.

The unit is divided into two electrical sections constructed in a straight line, and obviously operating in tandem. Each section contains

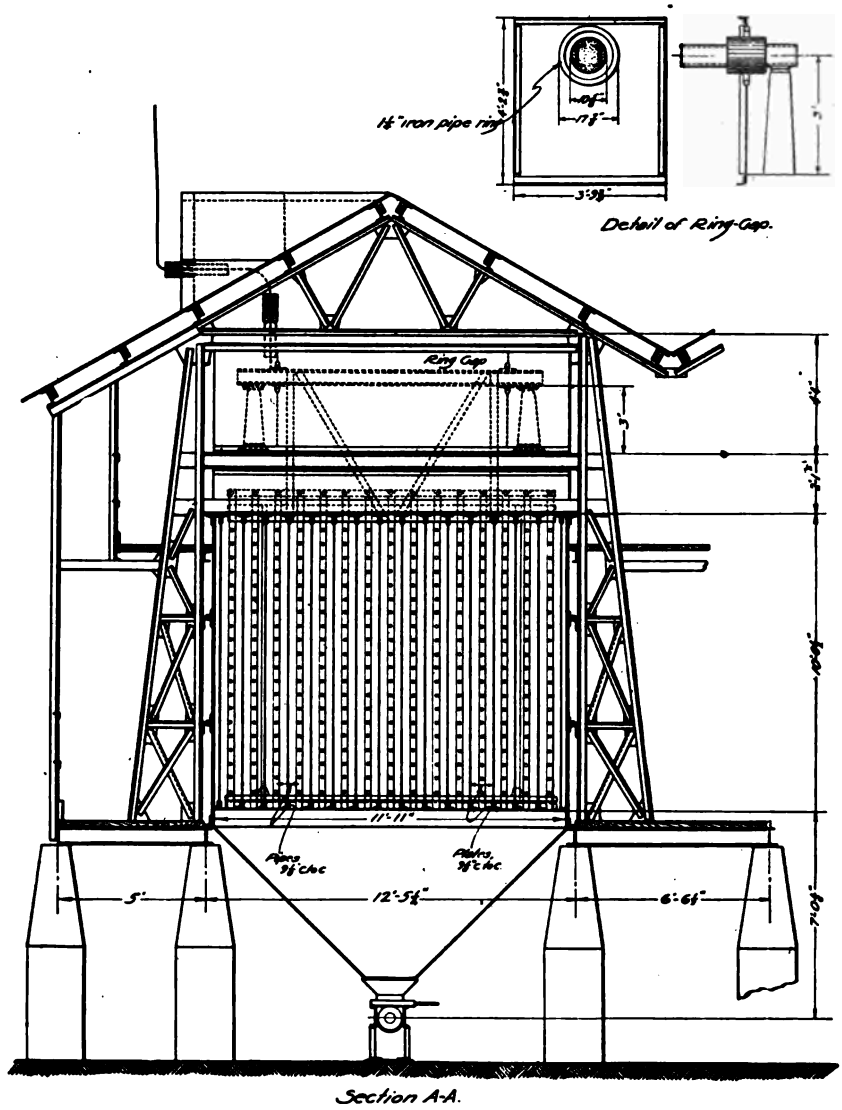


FIG. 2.—SECTION OF COTTRELL TREATER.

two 10-ft. (3-m) banks of plates, or an effective length of 20 ft. The pipe electrodes are 26 ft. long and extend through both banks of plates. These pipes are supported by three grids, one on each end and one in the middle

between the two banks of plates. The intermediate supporting grid is necessary to keep the sag of the pipes within allowable limits. The grid is built up with 1¼-in. (3-cm.) pipes that have been bored to allow the ¼-in. pipes to pass through, and is suspended from a beam carried on post insulators. A box encloses the insulators and the beam on top of the treater as shown in Fig. 2 The feed wire is brought into this box through an insulator bushing. Each insulator is completely enclosed in a small compartment which protects it from the gas stream.

The channel-iron beam that rests upon the insulators passes through ring gaps in the inside walls of these insulator compartments. The ring gap consists of an annular ring, made of a 1¼ in. (3-cm.) pipe bent into a ring with the ends welded together, which is welded to a round opening in the wall, and a short length of 10-in. (25-cm.) pipe slipped over the beam, making a 2-in. gap. The opening inside the 10-in. pipe is filled with cement.

Each row of corrugated iron sheets, forming the plates, is suspended, with the corrugations vertical, from the top by means of two angle irons back to back, which make a slot into which the sheets are inserted and secured with bolts. Practically the same arrangement is used at the bottom as a guide only. The sheets are not bolted to the bottom angles, nor are they fastened to one another. They must be carefully inspected before being put in the treater and only those free from warp used. The top of the treater is made of steel plate; and the side walls and the insulator house is ⅜-in. (9.5-mm.) transite board mounted on steel framework.

Knocking devices are provided for shaking the dust from the plates and pipes. For the former, there are four knockers, one in each space between insulator boxes. The knocker is composed of a shaft running transversely across the top of the treater, to which hammers are attached, one for each row of plates. The shaft is partly rotated by a handle attached to it, and the hammers strike the angles that support the plates, first on one side of the shaft and then on the other. The two pipe knockers are similar in design and are located to hit the under side of the middle grid of each electrical section. Small doors in the sides opposite the grids enable a man to enter the treater to make repairs if necessary.

The treater is supplied with a slide damper at the intake by means of which all smoke entering can be shut off, and with a butterfly damper at the outlet. There is a butterfly damper, also, in the section of the old flue used as a bypass. The intake is also provided with two sets of louvers, one having vertical and the other horizontal axes. At the outlet there is one set with horizontal axes. The purpose of these was to regulate distribution, but so far they have not been used.

Nine hoppers underneath the treater collect the dust. The ends as well as the sides of these hoppers come right up to the floor line and each is provided with a vertical baffle, which extends through the treater from the

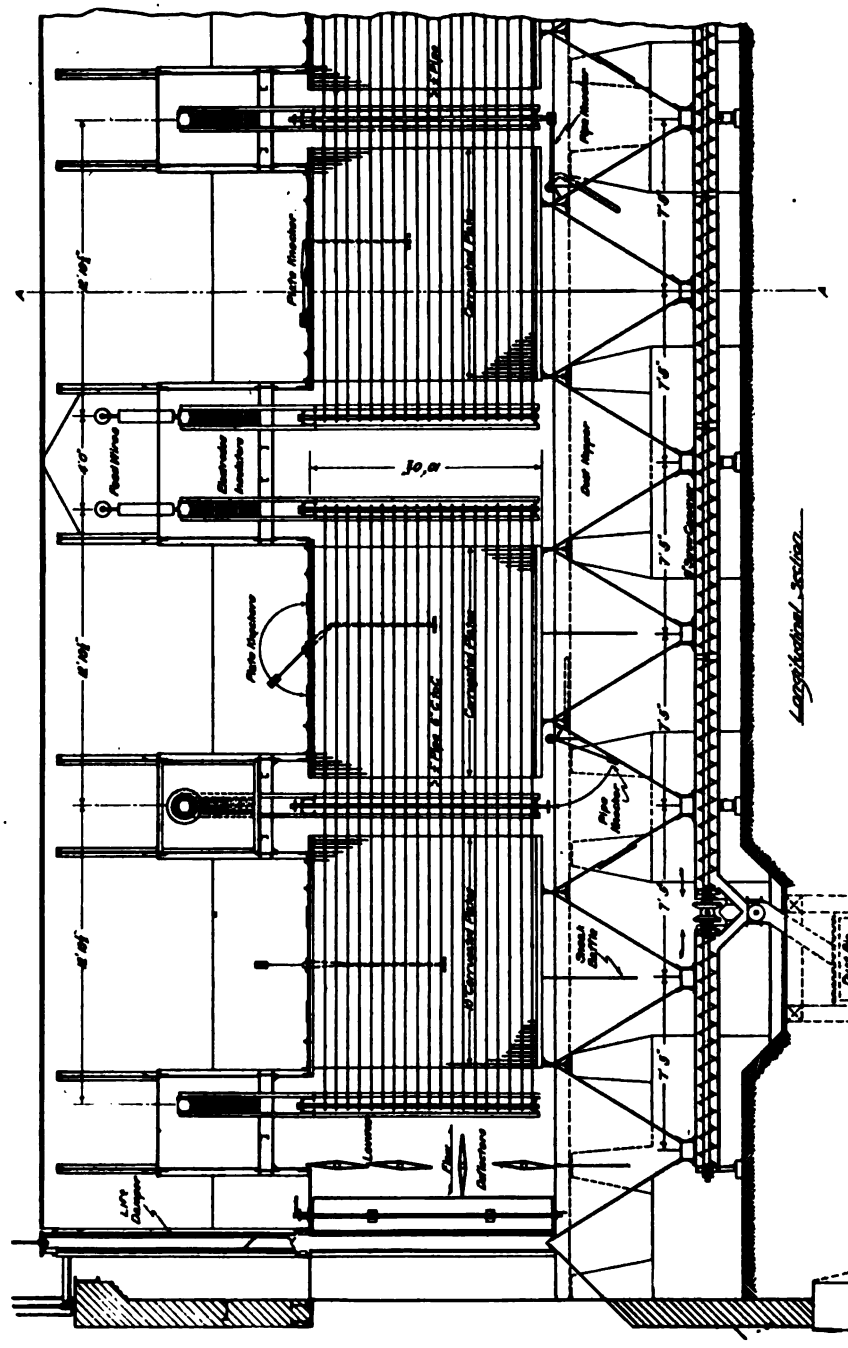


FIG. 3.—SECTION OF COTTRELL TREATER.

floor line nearly to the bottom of the hopper to prevent gas from sneaking through.

Electrical Equipment

The electrical equipment for each section is as follows: one 25 kv-a., 100,000 / 87,500 / 75,000 / 62,500 / 50,000 / –220-volt transformer; one 31-in. disk-type mechanical rectifier; one synchronous motor, 3-hp, 1800-r.p.m., 220-volt, three-phase, 60-cycle, for driving rectifier; one 37½ kv-a., 2200 to 220-volt transformer, single-phase; one 1.25-ohm grid resistor with current-carrying capacity of 100 amp., divided into seven sections; one, 2.75-kv-a., 60-cycle, 220-volt, 22-volt, 125-amp. motor-generator induction regulator; three, 7½-kv-a., 2200 to 220-volt single-phase transformers; one switchboard panel with necessary meters, etc.

In supplying power, the procedure at this treater follows that of the other Cottrell installations of the Tooele smelter, *i.e.*, to step down one phase from the smelter main power line, so that it can be handled on the switchboard, and put it directly on the treater transformer, using a synchronous motor to operate the rectifier. No motor-generator sets are used. The voltage is regulated by means of a grid resistor, the final adjustment being made by means of an induction regulator, thereby gaining much closer control of the voltage than can be obtained from use of the grids only.

Operation

In the operation of the treater, the pipes and plates are cleaned periodically. During the few minutes required for this work, the dampers at each end of the treater are closed and the gases bypassed. Accumulations of the collected dust not readily removed by the knockers have not been found to interfere with electrical conditions, nor with treater efficiency, probably due to its acid content and high electrical conductivity. After some time, this dust forms a rather thin permanent scale upon both plates and pipes which it is almost impossible to remove and which might, in appearance, be compared to boiler scale.

A number of aspiration tests have been made to determine the recovery obtained by the treater for actual gas velocities varying from 15 to 22 ft. per sec. through it. Typical recoveries for these velocities (there is very little variation in this range) are shown in the following table:

Metals	Per Cent. Recovered
Copper	98.2
Lead	81.2
Silver	96.5
Gold	96.4
Total Recovery	93.97

Velocity through treater (actual conditions of temperature and pressure), 21.45 ft. per sec. Volume through treater (actual conditions of temperature and pressure), 146,004 cu. ft. per min. Temperature at outlet, average 260° F. (127° C.) Temperature at inlet, average 280° F. (138° C.)

The uniformity of distribution is probably responsible, in a large measure, for the efficiency attained with the high velocity, which is approximately the equivalent of a 15 mi. per hr. breeze. The upper limit of velocity for 40 ft. of plate electrode has not been determined, but a material drop in recovery has been noted at 31 ft. per sec.

Mention has been made of the fact that advantage may be taken of the principle of selective precipitation in this type of Cottrell treater where the composition of the dust or fume is such that the recovery of several products is possible. Table 1 shows the distribution of the various components of the dust drawn from the successive hoppers underneath. The hoppers are numbered from the intake and toward the outlet.

TABLE 1.—*Analysis of Dust*

Hopper Number	Copper, Per Cent.	Lead, Per Cent.	Silver, Ounces per Ton	Gold, Ounces per Ton	Insoluble, Per Cent.	Iron, Per Cent.	Sulfur, Per Cent.	Lime, Per Cent.
1	8.30	3.2	6.84	0.45	19.7	18.7	14.3	2.6
2	8.30	3.7	6.26	0.44	20.6	17.1	14.0	2.6
3	7.60	5.3	6.82	0.38	20.0	17.3	14.0	2.5
4	7.00	6.8	6.96	0.34	19.2	15.3	14.7	2.3
5	6.00	8.2	5.94	0.30	16.8	13.4	14.7	2.1
6	5.15	11.6	5.90	0.27	16.1	12.3	14.0	2.2
7	4.55	13.1	5.36	0.24	13.5	10.2	15.5	1.7
8	3.95	15.5	4.80	0.19	11.4	8.7	15.2	1.5
9	3.80	14.8	4.30	0.19	10.3	8.4	16.2	1.7

The outstanding features are the constantly decreasing copper values and increasing lead values along the treater toward its discharge end, with the result that a portion of dust collected may be segregated and smelted for its lead content. An examination of the figures for iron and insoluble matter bears out the idea that there is a marked tendency to precipitate the true dust particles near the entrance, and that the more impalpable fumes must travel a greater length through the electric field before being caught.

It is extremely difficult to state, with any degree of accuracy, the power input into the treater, other than that it is much lower than one would expect and is quite variable. For normal gas volumes (125,000 to 150,000 cu. ft. per min.), the input of power will average close to 8.4 kv-a. for the first electrical section and 5.5 kv-a. for the second. Approxi-

nearly 85 per cent. of the dust caught is collected by the first and 15 per cent. by the second section. Secondary peak voltages run from [illegible] to [illegible], and occasionally higher; they are usually about [illegible] to [illegible] volts higher in the second than in the first section.

In conclusion, it may be said that the Cottrell installation has proved admirably adapted to these particular cases. Its ability to treat a purely fume product satisfactorily is an unsettled question, no data being available for its performance in this respect. However, when one studies

Fig. 4.—General view of [illegible] plant [illegible] smelter.

Fig. 4 and compares the compact flue-like building which is efficiently handling 150,000 cu. ft. of gas per minute, with the enormous towering structures of the vertical type necessary to treat this amount, one is convinced that a distinct step forward has been taken.

Credit should be given to Mr. [illegible], assistant general manager of the International Smelting Co., for the suggestion of the horizontal electrode and the use of pipes for this purpose, thereby making the application of the pipe-type treater to a horizontal flue feasible; to Mr. [illegible] Sumner, metallurgical superintendent of the Tooele smelter, for its design, and to Mr. [illegible], superintendent of the treat plant at the Tooele smelter, for the experimental work done in its development.

DISCUSSION

Harry V. Welch,* Los Angeles, Calif. (written discussion).—The basic requirements of the electrostatic process of electrical precipitation

* Western Precipitation Co.

is that gases containing solid particles in suspension are forced to pass through an electrical field consisting of an insulated high-potential wire, or other type of discharge member, and a grounded plate, or other type of collecting member. Commercial operation and efficiency of precipitation are secured by electrical and structural arrangements to provide the maximum value of the variable factors modifying the degree of precipitation. That is to say:

1. A unidirectional flow of high-potential current is vastly more effective in precipitation than a high potential alternating-current flow.

2. Superior precipitation is secured with the discharge wire or member of negative polarity.

3. Maximum efficiency is secured by operation at the highest practical voltage; that is, at a voltage just below the point at which continuous arcing takes place.

4. The voltage gradient between the discharge electrode and the grounded electrode should be as steep as the condition of the gases and deposit will permit. Poor precipitation, in general, is secured at 5000 volts drop per linear inch but few plants are able to continuously exceed a voltage gradient of 15,000 volts per linear inch. Average plant voltages for continuous operation range between 7000 and 14,000 volts.

5. Dust and fumes, in general, show greatly different characteristics of precipitability; one explanation may be: Dust particles, in comparison with fume particles, are of enormous size and possess angles, faces, and edges; as a result they easily receive a static charge and are attracted by the receiving electrode, to which they adhere and of which they become an integral part, so far as electrical conditions are concerned. Fume particles, however, are totally different in nature; they are formed by the chilling to a solid form of a metallic carrying vapor by contact with surfaces or walls. They are, at first, almost infinitesimally small, probably amorphous, and possibly spherical in form. These minute particles apparently condense a film of air or gas about themselves, or possibly absorb gases, which greatly modify their electrical precipitation characteristics. Analysis of various fume samples (which also contain more or less dust) have indicated a condensed-air content of from ½ to 4 per cent. by weight.

Fume particles are much more difficult to precipitate than simple dust. One requirement seems to be the necessity of a greatly increased current input, which is dissipated from the discharge electrode and provides the means for the voluminous ionization necessary to charge the fume particles. It seems probable that the charging of suspended particles is effected by the addition or adsorption of ions by the floating particles, and that where fume is encountered, the condensed envelope of gas around a fume nucleus, or particle, increases greatly the difficulty of ionic charging and that a greater quantity of current must be dissipated

into the gases for fume collection than is required for dust. In commercial practice, increased ionization of gases has been secured by decreasing the size of the discharge member; that is, by using fine wires rather than heavy wire, light chain, bars, or small pipes.

Two strikingly different effects due to precipitated film of fume upon the walls of the collecting pipes or plates have been observed where the gases are neutral in character (for example, metallurgical fumes containing much zinc and lead) and where the temperature has been too high to speak of relative humidity, or where the humidity of the gases has been below 40 to 60 per cent. of saturation. In the one case the deposit, noted particularly in a lead smelter, apparently blanked off a good portion of the surface of the collecting electrode, and through certain spot areas and points on the collecting surface caused intensely active ionization or current flow points, or localized areas, which neutralized the relative ratio of the superficial area of discharge to collecting electrodes and induced "back ionization" or "back discharge" from the collecting electrode. The result of this back discharge was a heavy current flow between the discharge terminal (wire or small chain) and the collecting terminal (plate or pipe) with a consequent drop in effective potential gradient to a point below which effective precipitation is secured. The second effect was noted in a laboratory test with zinc-oxide fume in a dry gas and at common stack temperature. The deposit was so coherent and so effective an insulator that as the deposit formed the current reading decreased and the potential increased until so little ionization resulted that effective precipitation was no longer obtainable.

Since with basic fumes, such as are produced in lead smelters and zinc-oxide plants, it is usually impracticable to secure an acid condition of the gases, good precipitation has been secured by cooling and humidifying the gases and fumes by water sprays. The moisture content of the gases, when present at from 40 to 60 per cent., or higher, of saturation, apparently adversely affects the condensed gas envelope surrounding the fume particles, rendering them more susceptible to ionization and thus yielding a precipitated deposit which functions electrically as integral with the collecting electrode.

6. Power input into a given treater varies greatly with the physical conditions of gas, suspended particles encountered, and temperature prevailing. For any specific installation and constant condition as to gas, suspended particles, and temperature, the input may be said to increase with the total length of effective discharge electrode and to decrease as the diameter of the discharge electrode is enlarged.

7. In the study and design of Cottrell precipitators, it has been found that the length of effective discharge electrodes per unit is more a measure of the capacity of that unit than, for example, the cross-sectional area or the superficial surface exposed by the collecting electrode. As a corollary

to the above, so long as the proper ratio of volume of gas treated to discharge electrode provided is maintained, the size of pipe or plate spacing, within reasonable limits, is immaterial; and so long as the gas velocity, which will vary inversely as the spacing, does not rise until the mechanical scouring effect is sufficient to remove appreciable quantities of the precipitated deposit. Experience with cement-plant potash fumes has indicated that loss due to the scouring action becomes appreciable around gas velocities of 8 to 16 ft. per sec. and rapidly increases with increased gas velocity.

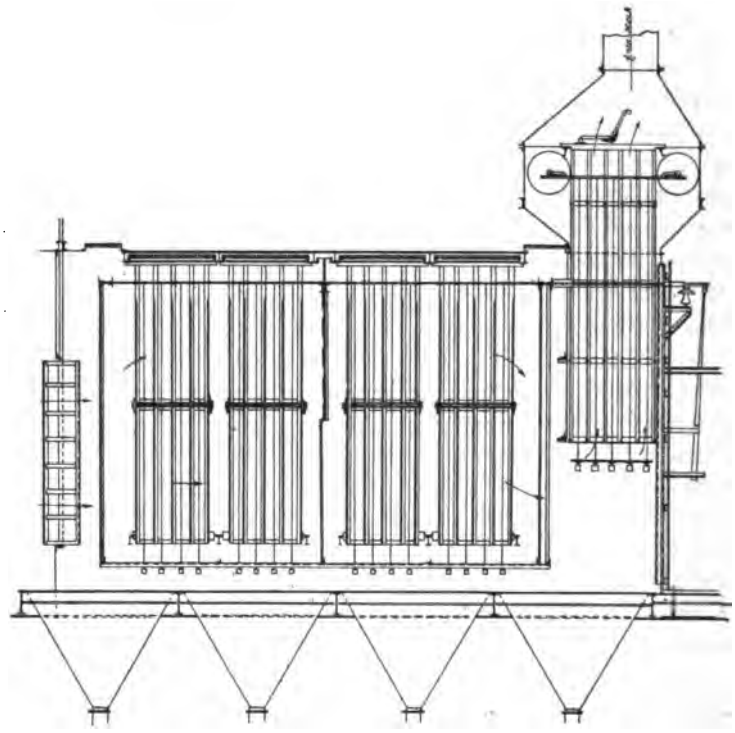


FIG. 5.—LONGITUDINAL SECTION OF COTTRELL TREATER AT PORTLAND CEMENT PLANT.

8. Efficiency of precipitation is greatly affected by the distribution of the gas velocity throughout the effective cross-sectional areas of the Cottrell. The maximum efficiency is secured with uniform gas velocity: uneven gas velocity through plate or pipe always results in lower collection, even when the mean velocity is satisfactory.

The precipitator described by Mr. Young takes advantage of the various principles developed for precipitation work. It provides a high ratio of linear feet discharge wire per quantity of gas treated; and as the suspended particles are practically free from fume, are more or

less coarse, and are carried in a gas stream containing sufficient acidity to facilitate the precipitation operation, it is possible to use fairly large diameter discharge electrodes, which make possible their easy and satisfactory arrangement in a horizontal position. The construction of treaters in series has both advantages and disadvantages. The

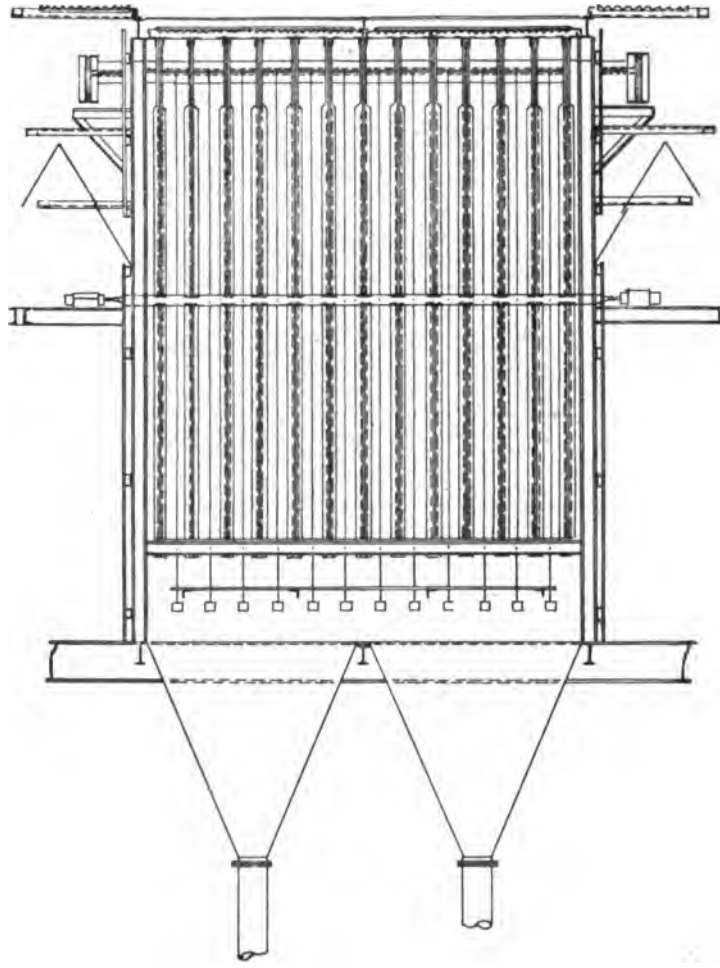


FIG. 6.—CROSS-SECTION OF COTTRELL TREATER AT A PORTLAND CEMENT PLANT.

advantages, as Mr. Young points out, lie in the simplicity of gas distribution, avoidance of turns and deflections of the gas stream, and uniformity of velocity through all parts of precipitator apparatus. A construction having, in general, these same advantages was utilized in the construction of the Cottrell treater for the Riverside Portland Cement Co. at Crestmore, Calif.

As shown in Figs. 5 to 7, vertical hanging discharge wires were used. Vertical wires permit the incorporating, in a horizontally operating treater, of small baffle angles on the walls between the discharge wire to prevent "creepage" of the collected material along the plates in a direction parallel with the gas flow at comparatively low gas velocity, and of checking the "scouring" effect where higher gas velocities are utilized. Vertical discharge members permit greater flexibility in the diameters of the discharge members; in the tests and plant, the diameters of these members have varied from a few hundredths of an inch to several inches.

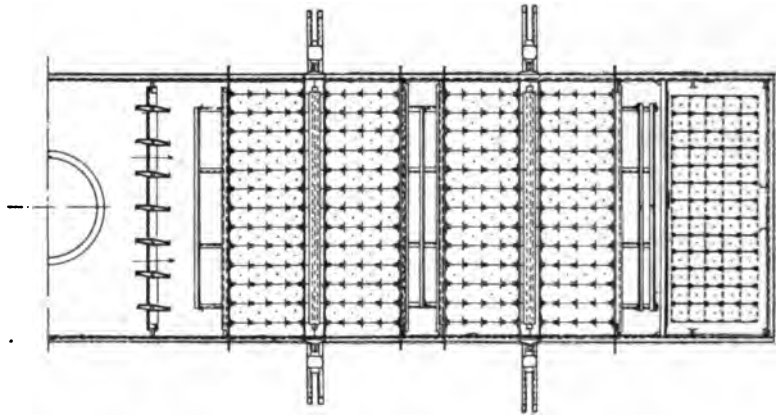


FIG. 7.—PLAN OF COTTRELL TREATER, ETC.

The disadvantages in a series operating Cottrell plant are: In order to effect repairs in one unit, the entire Cottrell precipitator must be taken out of commission; the removal of the deposited dust from the plates or pipes by rapping is effected in a gas stream moving at high velocity, which results in final losses to the stack. Cottrell units operating in parallel at approximately 98 per cent. efficiency, will fall to approximately 90 per cent. efficiency when one-half of the units are cut out for rapping or repairs and each unit is receiving approximately twice its normal volume of gas. In general, a number of units are operated in parallel, each unit in turn being shut off by dampers and the deposit shaken down. With fumes and fine dusts, the quiescent gas zone, afforded by closed inlet and outlet dampers to a precipitator unit, seem most essential for efficient and satisfactory collection into the hoppers. For the conditions at the International Smelter plant, the Tooele flue-type Cottrell yields remarkably good results, and credit is due the officials and technical staff for their thorough preliminary test work and excellent plant construction.

Fractional or selected precipitation, which functions in a most advantageous manner at the Tooele plant, has been noted in several other installations of the plate type. The main sections of the treater at the Riverside Portland Cement Co.'s plant consists of four sets of screen plates in series. Four samples to each plate are taken in progressive series across the plates, making sixteen in all. These show the progressive decrease in lime content and increase of potash content given in Table 2 and in Fig. 8. The potash content is largely in the form of fume, so its collection is not effected as easily as the dust is thrown from the dust-laden gas stream. Analyses by hoppers also indicated a marked selective action upon the potash collection, as follows:

Hopper No.	Per Cent. K_2O
1	1 to 4
2	5 to 8
3	9 to 12
4	13 to 16

TABLE 2.—*Analysis of Dust Samples From Longitudal Section of Plate-type Precipitators in Cement Factory*

Sample	Plate Section	Per Cent. CaO	Per Cent. K_2O
1	I	46.5	3.51
2		44.3	3.86
3		39.3	4.30
4		35.65	5.11
5	II	39.7	7.63
6		29.1	6.65
7		26.9	7.24
8		33.9	7.34
9	III	32.8	9.96
10		31.8	8.40
11		30.7	9.80
12		28.7	13.04
13	IV	25.4	15.98
14		20.9	16.02
15		22.4	19.32
16		17.7	18.90

Y. A. RULE, El Paso, Texas (written discussion).—The writer suggested the plate-type treater to Mr. O. M. Kuchs, in 1916, while assistant superintendent of the Tooele smelter. Realizing the expense of constructing the pipe treater and its limitations in recovering variable amounts of fume and dust under different gas speeds and temperatures, it was thought that if sets, or banks, of plates were arranged in a flue so that the

gases would receive a serial treatment, all solids, practically possible, could be removed. For a gas from which the solids are hard to recover, as many sets of plates as necessary would be used; in the case of an easily treated gas, the current could be cut off from one or more of these sets. In the placing of the plates and wires (or pipes), the distance between plates and wires does not have to follow rigid rules of construction for the plates and wires can be set in grid form so that the spacing can be regulated at the will of the operator.

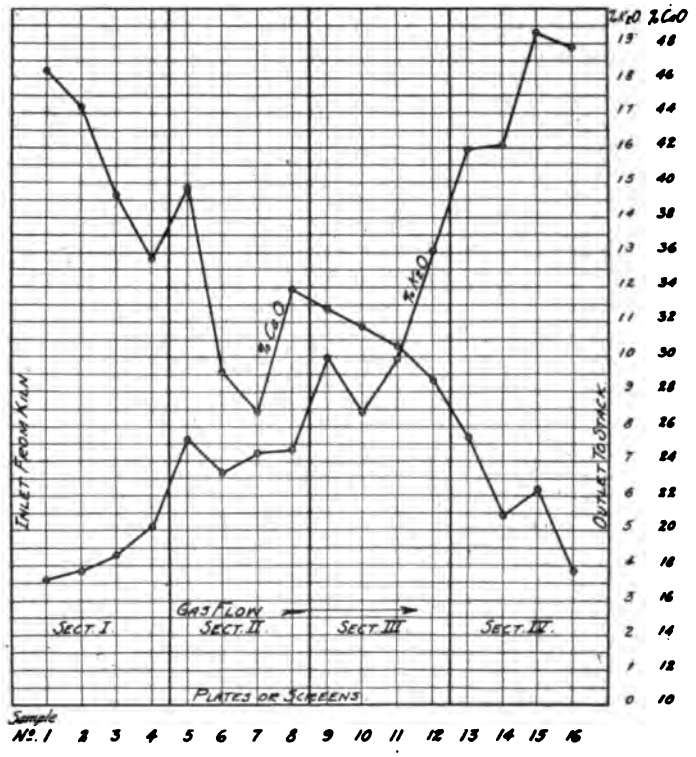


FIG. 8.—ANALYSIS ALONG LONGITUDINAL SECTION OF PLATE COTTRELL PRECIPITATOR, CEMENT FACTORY.

In localities where steel is expensive or other semi-non-destructible building material is cheaper, the flue of rectangular cross-section will answer very well, but the effect of acid, moisture, and heat must always be kept in mind when choosing the material to be used.

To make the arrangement of the plate type of treater plant most convenient, two flues of the same cross-section leading from a chamber and joined beyond the last set of plates in each flue can be used. Outside of the additional length of flue and plate sets, the one power house operates on the gases continuously through either flue.

This type of treater should be much more adjustable to the treatment of gases than the pipe treater and will probably cost 30 to 50 per cent. less for construction and operation when large plants are to be considered.

A. A. HEIMROD, New York, N. Y.—To handle about 20,000 cu. ft. of gas at a temperature of about 1000° F. requires nearly 30 tons of steel for the structure itself, casing and supports; about 120,000 bricks for the lining of the precipitator, and about 30 tons of interior parts (that is, collecting and discharging electrode system, roof and supporting members) also 15 tons of castings, parts used on the interior members which are subjected to the extremely high temperature.

The power consumption depends on whether fume or dust is collected. In one plant, where only dust particles were treated, the power consumption was not more than 3 kw. In another plant, having exactly the same kind of precipitator, where the collected material was fume, the power consumption jumped from 3 to nearly 10 kilowatts.

Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals

By W. P. Sykes,* Cleveland, Ohio

(New York Meeting, February, 1921)

This investigation was undertaken primarily to establish the relations existing between temperature and mechanical properties in molybdenum, nickel, and an aluminum-copper alloy. Molybdenum (m.p. 2500° C.) was chosen because it is partly similar to tungsten and partly similar to the common ductile metals. Also it is known to furnish, by proper treatment, a desirable material to use in studying relation of grain size and physical properties. The molybdenum used was of the quality that is drawn into wire 0.003 in. in diameter for use as filament supports in incandescent lamps; chemical analysis shows less than 0.1 per cent. of impurities.

Nickel belongs to the same class as iron. Its melting point is 1450° C. and an allotropic change at about 370° C. results in a loss of magnetism above that temperature. This feature made nickel doubly valuable for the purposes of these tests. The nickel used was obtained from the Driver-Harris Co. as 0.090 in. (2.3-mm.) wire, annealed; analysis showed 99.8 per cent. nickel and 0.150 per cent. iron.

Aluminum is one of the low melting-point metals. Some tensile tests at elevated temperatures have been reported by Bengough but the possibility of learning more with the low temperature and sensitive apparatus available recommended this metal. The samples marked Al are an aluminum-copper alloy that contains 3 per cent. copper, 0.42 per cent. iron, and 0.21 per cent. silicon. The presence of the copper somewhat complicates the analysis of the results; but the action of copper in aluminum has been studied so that its influence might have been foretold, in part at least. The material and analyses were furnished by the Aluminum Castings Co.

The nickel wire, which was deformed at 400° C., was drawn under a bath of molten lead and through a die, which also was immersed in the bath. A thermocouple was suspended in the molten metal to indicate the temperature. Hot oil was used as the heating bath for drawing the

* Metallurgist, Cleveland Wire Div., National Lamp Works.

aluminum wire at 175° C. This temperature was controlled by a mercury thermometer. The heat in both cases was supplied by gas burners.

The interpretation of the curves shown is based on the amorphous-cement theory and the hypothesis of a temperature of equal cohesion for any metal.

Methods of Tests and Description of Apparatus

In this investigation measurements were made of the tensile strength, reduction of area, and elongation (per cent. in 2 in.). No accurate

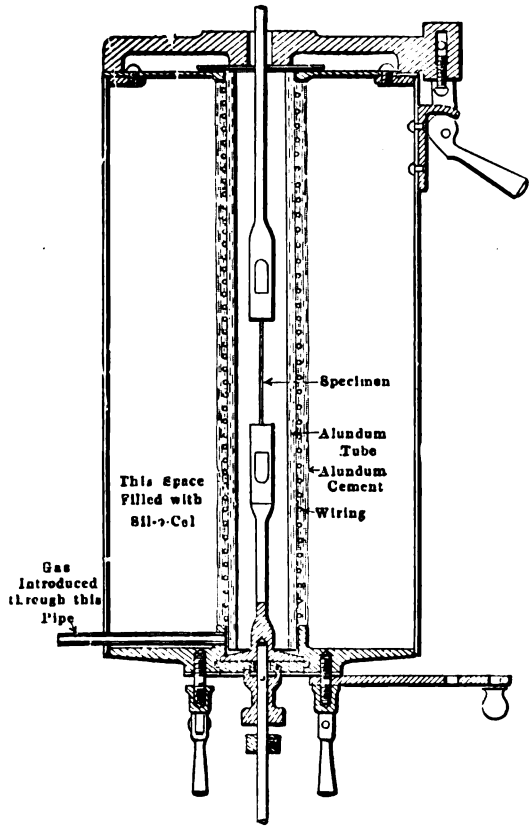


Fig. 1.—Detail of furnace.

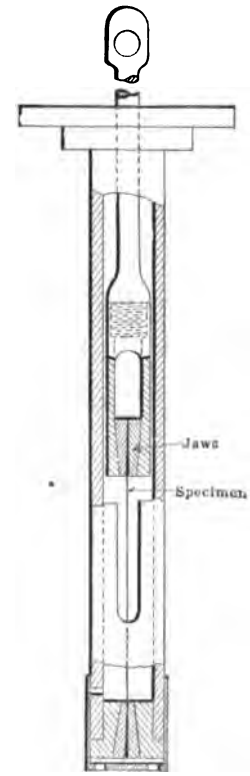


Fig. 2.—Detail of tube with specimen in position.

method of determining the elastic limit was available. The apparatus used was described by Jeffries.[1]

Fig. 1 shows the furnace used for tests at temperatures above 240°.

[1] Zay Jeffries: Effect of Temperature, Deformation, and Grain Size on the Mechanical Properties of Metals. *Trans.* (1919) **60**, 474.

It consists of an alundum tube, 1 in. (2.54 cm.) inside diameter and 12 in. long, wound with nichrome ribbon and fitted into a steel cylinder with heat insulation between the tube and cylinder as shown. The test piece is secured in the jaws and drawn into position by a wire passed through the furnace from above. A flange on the bottom clamp fits snugly into a seat at the bottom of the furnace, a hinged plate is then closed under the base of the flange; at the top of the heating tube, the extension of the upper clamp passes snugly through a hole in the furnace covering. The atmosphere within the furnace is thus easily brought to the desired temperature without interference by external air currents.

All tests at temperatures above 600° C. were conducted with the test piece in an atmosphere of argon gas to prevent any harmful effect of oxidation. For tests at lower temperatures the furnace is replaced by the steel tube shown in Fig. 2.

FIG. 3.—NI-1. NICKEL REDUCED 93 PER CENT. BY WORKING AT ROOM TEMPERATURE. × 250.

All specimens were marked by scratching the surface with diamond points set exactly 2 in. (5.08 cm.) apart. The wire was then fitted into the clamps, leaving about 2½ in. between the upper and the lower heads.

Two rates of loading were used with most of the specimens. The slow one, by which the upper jaw was lifted at the rate of 0.125 in. per min., and the rapid one by which it was moved 1 in. per min. All tests in which the rates of loading were different are so designated in the tables.

Liquid-air Tests.—The tube and clamps enclosing the test pieces were immersed in a vacuum jar containing liquid air. After the piece was cooled to the temperature of the liquid, as indicated by the cessation of boiling, the load was applied and the piece broken. The jar of liquid air was then replaced by one full of warm water, to make possible the rapid removal of clamps and test piece.

Tests at −50° C.—This temperature was attained by the use of ether

and carbon-dioxide snow, contained in a vacuum jar. The temperature varied about 10° C. on either side of −50° C. during the series of tests. These temperatures were measured with a pentane thermometer.

Tests at 100°, *and* 200° *to* 240° *C.*—To maintain a temperature of 100° C., the test specimen was kept immersed in boiling water contained in a vessel upon an electric hot plate supported on the frame of the testing machine.

In the tests at 200° and 240° C. melted crisco was used as a heating bath. The liquid was contained in a vessel upon an electric hot plate and the temperature was determined by a mercury thermometer.

Measurement of Elongation.—The wires were marked by scratches 2 in. apart; after a piece broke in tension the length between marks was

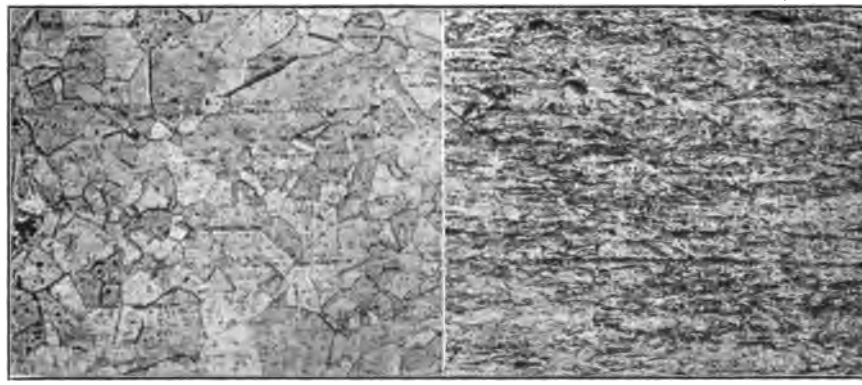


FIG. 4*a*.—NICKEL (0.040 IN.) ANNEALED AT 800° C. FOR 1 HR. × 250.

FIG. 4*b*.—NI-3. NICKEL DRAWN FROM 0.040 IN. TO 0.025 IN. × 250.

measured. Very few breaks occurred at the marks and in most cases these have been discarded. The elongation was only slightly affected by a break outside the marks, but these breaks have not been included in the tables.

Reduction of Area Measurements.—The diameters at the point of break were measured under a microscope and a micrometer eyepiece at a magnification of 30 diameters. The reduction of area was computed from the mean of several measurements. These measurements may be subject to an error of 5 per cent.

DESCRIPTION OF MATERIAL TESTED

Mo-1.—Molybdenum wire 0.025 in. in diameter produced by swaging a rod 0.125 in. to 0.035 in. and drawing from 0.035 in. to 0.025 in. diameter. The working temperatures were gradually lowered from about 1300° C. at the larger sizes, to about 1000° C. at the smaller sizes; this represents a 93 per cent. reduction of cross-section by working.

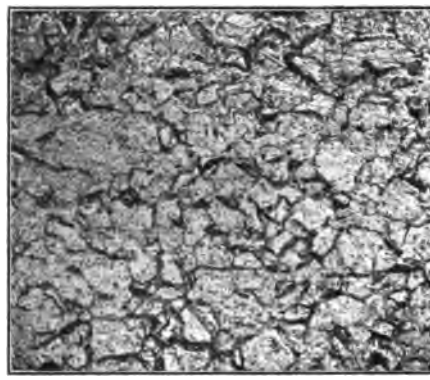


FIG. 5.—Ni-2. NICKEL ANNEALED AT 800° C. FOR 30 MIN. × 300.

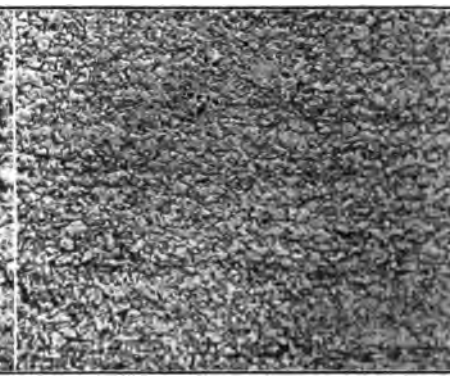


FIG. 6.—Ni-1-700-B. Ni-1 AFTER TENSILE TEST AT 700° C. × 250.

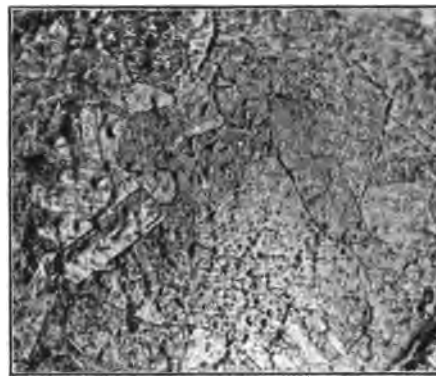


FIG. 7.—Ni-2 AFTER TENSILE TEST AT 1000° C × 250.

FIG. 8.—Mo-3. MOLYBDENUM ANNEALED AT 0.040 IN. AND DRAWN TO 0.025 IN. DIAMETER. × 250.

FIG. 9.—Mo-5. 0.025-IN. MOLYBDENUM WIRE ANNEALED IN HYDROGEN AT 90 PER CENT. OF ITS FUSION AMPERAGE FOR 5 SEC.; 1100 GRAINS PER SQUARE MILLIMETER. × 250.

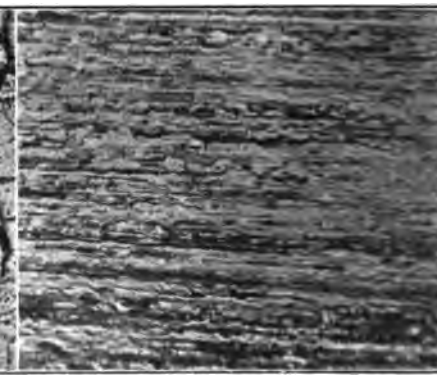


FIG. 10.—Mo-6. 0.025-IN. MOLYBDENUM WIRE ANNEALED TO GIVE STRUCTURE OF FINE GRAINS; 35,000 GRAINS PER SQUARE MILLIMETER. × 500.

Mo-2.—Same material and degree of working as Mo-1. Temperatures of working ranged from 800° C., at the start, to a black heat at the finish.

Mo-3.—Molybdenum wire drawn from 0.045 in. to 0.025 in. diameter

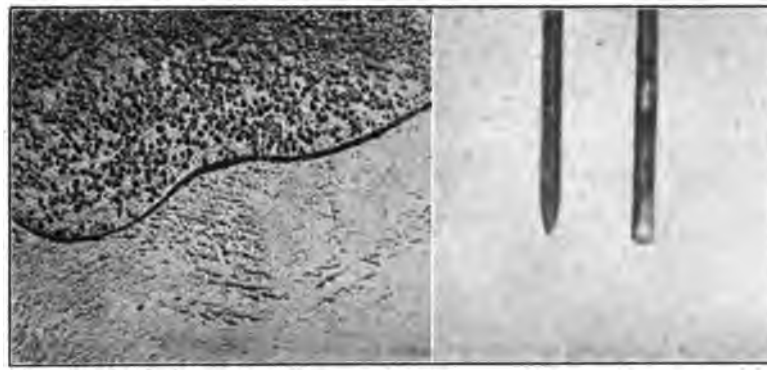


FIG. 11.—Mo-7. 0.025-IN. MOLYBDENUM WIRE TREATED TO DEVELOP LARGE GRAIN SIZE. × 250.

FIG. 12.—FRACTURE OF Mo-7 (COARSE GRAIN) DURING TENSILE TEST AT 300° C.; "WEDGE" REDUCTION AND DIRECTIONAL EFFECT SUGGEST ANISOTROPIC CRYSTAL. × 7.

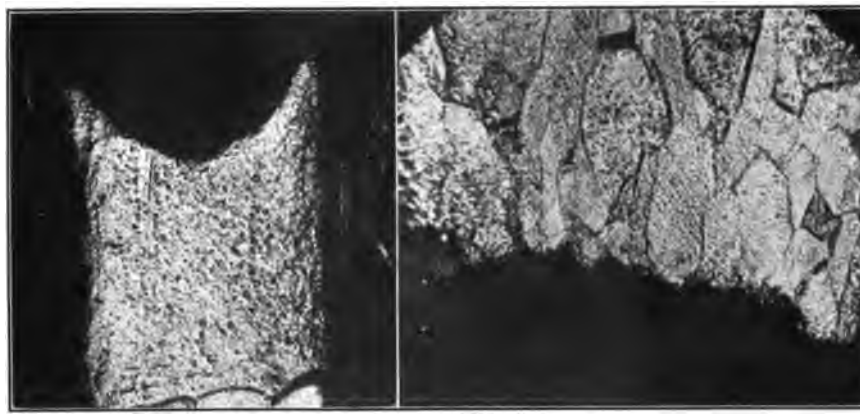


FIG. 13.—FRACTURE IN TENSILE TEST AT ROOM TEMPERATURE OF COARSE-GRAIN MOLYBDENUM (Mo-7); PATH OF RUPTURE IS APPARENTLY ALONG GRAIN BOUNDARY. × 100.

FIG. 14.—SECTION THROUGH FRACTURE OF MOLYBDENUM WIRE (Mo-5) BROKEN IN TENSION AT 300° C.; PATH OF RUPTURE PASSES THROUGH THE GRAINS. × 100.

at temperatures of 1300° C. to 1000° C. The reduction by working on this material is 70 per cent.

Mo-4.—Same material and degree of working as Mo-3; temperature of working ranged from 800° C. to black heat.

Mo-5.—Molybdenum wire 0.025 in. in diameter annealed by heating in hydrogen for 5 sec. at 90 per cent. of the amperage required for its fusion. There are about 1100 grains to the square millimeter; the average diameter of the grains is 0.030 mm. (0.0011 in.); see Fig. 9.

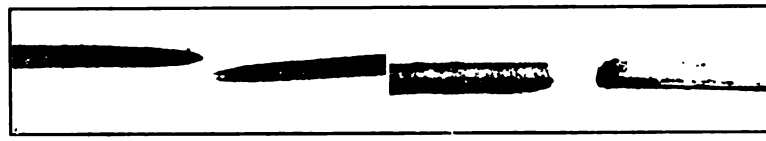


FIG. 15.—AL-7-600-B. FRACTURE OF ALUMINUM WIRE BROKEN IN TENSION AT 600° C.; NOTE EXTENT OF "NECKING" ALSO SHARP REDUCTION AT POINT OF FRACTURE. × 8.

FIG. 16.—Al-2-630-A. FRACTURE OF ALUMINUM WIRE BROKEN IN TENSION AT 630° C.; NOTE ABSENCE OF REDUCTION OF AREA AND SUGGESTION OF INTERCRYSTALLINE FRACTURE. × 8.

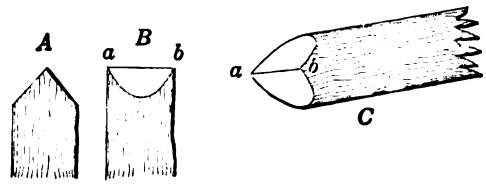


FIG. 17.—REDUCTION OF AREA AT AND ABOVE 300° C. IN COARSE-GRAINED MOLYBDENUM (Mo-7). *A* AND *B* ARE BOTH LONGITUDINAL VIEWS; IN *B*, PIECE HAS BEEN TURNED THROUGH AN ANGLE OF 90° FROM POSITION *A*. EDGE *a-b* IS RESULT OF COMPLETE REDUCTION IN DIRECTION OF ONE AXIS.

FIG. 18.—Mo-1-200. REDUCTION OF AREA AT POINT OF FRACTURE IN WORKED MOLYBDENUM WIRE (Mo-1); TESTED AT 200°. × 100.

Mo-6.—Molybdenum wire 0.025 in. in diameter annealed for 3 sec. in hydrogen at 65 per cent. of its fusion amperage. The grain size is extremely small; there being about 35,000 grains to the square millimeter; the average diameter of the grains is 0.0053 mm. (0.0002 in.); see Fig. 10.

Mo-7.—Molybdenum wire 0.025 in. in diameter. The extremely large grains in this wire were produced in the following manner: At

0.027 in. diameter the wire was equiaxed by heating in hydrogen for 5 sec. at 90 per cent. of its fusion amperage. This wire was then, at a low red heat, drawn through a 0.025-in. die and its cross-section reduced about 14 per cent. The wire was again heated in hydrogen. Many of the grains extend completely across the diameter of the wire and may be 0.5 in. in length; see Fig. 19. The average diameter of the grains may be taken as 0.34 mm. (0.013 in.); see Fig. 11.

FIG. 19.—LONGITUDINAL SECTION OF Mo-7 TESTED AT 300° C.; *A* AT POINT OF FRACTURE AND *B* ABOUT ¾ IN. FROM POINT OF FRACTURE.

Ni-1.—Nickel wire 0.025 in. in diameter was produced by drawing at room temperature from 0.095 in., the reduction being 93 per cent.; see Fig. 3.

Ni-2.—Same as Ni-1 but annealed at 0.025 in. for 30 min. at 800° C.; the resulting structure is shown in Fig. 5.

Ni-3.—Nickel wire drawn from 0.040 to 0.025 in. in diameter at room temperature; a reduction by working of 61 per cent. The annealed wire 0.040 in. in diameter is shown in Fig. 4*a* and when drawn to 0.025 in. diameter in Fig. 4*b*.

Ni-5.—Same as Ni-3 but drawn at 400° C.

Al-1.—Wire of aluminum-copper alloy drawn from 0.090 to 0.025 in. in diameter at room temperature; a reduction of 93 per cent.

Al-2.—Same as Al-1 but annealed at 400° C. for 15 min.

Al-3.—Wire of aluminum-copper alloy drawn from 0.040 to 0.025 in. in diameter at room temperature; a 61 per cent. reduction.

Al-4.—Same as Al-3 but drawn at a temperature of 175° C.

Al-7.—Same as Al-1 but annealed at 0.025 in. in diameter for 30 min. at 300° C.

TABLE 1.—*Mechanical Properties at Various Temperatures of Nickel Wire (Ni-1) Drawn Cold from 0.095 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Ni-1-L-A	−185	155,000		3.12		54		
Ni-1-L-D			162,000		2.30		52	
Ni-1-R-A	25	133,000		1.06		58		
Ni-1-R-B			135,000		1.06		58	
Ni-1-100-A	100	129,000		0.80		52		
Ni-1-100-B			132,000		1.15		56	
Ni-1-200-A	200	121,000		0.00		52		
Ni-1-200-B			122,000		0.00		52	
Ni-1-300-A	300	119,000		0.00		58		
Ni-1-300-B			122,000		0.00		52	
Ni-1-400-A	400	107,000		0.00		56		
Ni-1-400-B			109,000		0.00		55	
Ni-1-500-A	500	87,000		0.80		63		
Ni-1-500-B			92,000		0.80		60	
Ni-1-600-A	600	83,000		0.80		55		Argon atmosphere
Ni-1-600-B			83,000		0.80		60	
Ni-1-700-A	700	22,000		18.5		82		
Ni-1-700-B			27,000		11.5		80	
Ni-1-800-A	800	13,000		15.5		65		
Ni-1-800-B			16,000		15.5		52	
Ni-1-900-A	900	8,500		20.0				
Ni-1-900-B								
Ni-1-1000-A	1050		5,700		25.0		52	

TABLE 2.—*Mechanical Properties at Various Temperatures of Nickel Wire (Ni-2) Drawn Cold from 0.095 to 0.025 In. and then Annealed at 800° C.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Ni-2-L-A	−185		86,000		22.0		58	
Ni-2-L-C			82,000		22.0		58	
Ni-2-R-A	25	60,000		22.0		75		
Ni-2-R-C			62,000		23.5		75	
Ni-2-100-B	100	56,000		20.3		73		
Ni-2-100-C			57,000		20.3		71	
Ni-2-200-A	200	50,000		15.5		68		
Ni-2-200-B			51,000		18.7		75	
Ni-2-300-A	300	50,000		18.0				
Ni-2-300-B			51,000		14.0		79	
Ni-2-300-D		50,000		17.0		75		
Ni-2-400-A	400	43,000		17.25		75		
Ni-2-400-B			47,000		19.5		80	
Ni-2-500-A	500	34,000		19.5		75		
Ni-2-500-B			36,000		20.0		75	
Ni-2-600-A	600	25,000		15.5		65		Argon
Ni-2-600-B			29,000		19.5		60	atmosphere
Ni-2-700-A	700	17,000		15.5		60		
Ni-2-700-B			21,000		14.0		60	
Ni-2-800-A	800	13,000		15.5		45		
Ni-2-800-B			17,000		15.5		48	
Ni-2-900-A	900	9,000		15.5		39		
Ni-2-900-B			11,000		20.0		48	
Ni-2-1000-A	1000	7,000		26.5		48		
Ni-2-1000-B			9,000		19.0		43	

MECHANICAL PROPERTIES OF NICKEL WIRES

Tensile Strength

The maximum tensile strength developed by the four samples of nickel wire is shown by Ni-1, which has been reduced 93 per cent. by working at room temperature. At the temperature of liquid air, it possesses a tensile strength of 158,000 lb. per sq. in. This maximum value may be regarded as the result of the following factors: First, the comparatively large amount of amorphous metal that, by the severe working, has been generated at the slip planes of the original grains of crystalline material; second, the cohesion of this amorphous network, so placed as to form a

TABLE 3.—*Mechanical Properties of Ni-2 (Annealed Nickel) Wire at Temperatures between 270° and 370° C.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Ni-2-270-B	270		49,000		15.00			
Ni-2-270-A		49,000		16.5		79		
Ni-2-330-A	330	48,000			17.00		79	
Ni-2-330-B			49,000	15.8		75		
Ni-2-370-A	370	47,000		16.5		83		
Ni-2-370-B			47,000		16.75		80	

TABLE 4.—*Mechanical Properties at Various Temperatures of Nickel Wire (Ni-3) Drawn Cold from 0.040 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Ni-3-L-A	−185	145,000		3.15		60		
Ni-3-L-B			147,000		3.15		54	
Ni-3-R-A	25		125,000		1.86	70		
Ni-3-R-C		124,000		1.06			70	
Ni-3-100-A	100	122,000		0.8		65		
Ni-3-100-C			123,000		0.8		75	
Ni-3-200-A	200	116,000		0.0		60		
Ni-3-200-B			116,000		0.8		67	
Ni-3-300-A	300	111,000		0.0		75		
Ni-3-300-B			112,000		0.8		75	
Ni-3-400-A	400	96,000		0.8		73		
Ni-3-400-B			98,000		0.8		75	
Ni-3-500-A	500	85,000		0.8		69		
Ni-3-500-B			85,000		0.8		76	
Ni-3-600-A	600	83,000		0.8		65		Argon
Ni-3-600-B			83,000		0.8		69	atmosphere
Ni-3-700-A	700	20,000		20.3		50		
Ni-3-700-B			27,000		17.0		71	
Ni-3-800-A	800	17,000		20.5		45		
Ni-3-800-B			19,000		18.0		40	

TABLE 5.—*Mechanical Properties at Various Temperatures of Nickel Wire Drawn from* 0.040 *to* 0.025 *In. at* 400° C.

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Ni-5-L-A	−185	129,000		3.15		55		
Ni-5-L-B		130,000		4.80		45		
Ni-5-R-A	25	110,000		3.12		73		
Ni-5-R-C			113,000		3.12		73	
Ni-5-100-A	100	104,000		2.35		73		
Ni-5-100-C			104,000		3.10		73	
Ni-5-200-A	200	98,000		2.35		73		
Ni-5-200-B			98,000		2.35		73	
Ni-5-300-A	300	86,000		1.55		68		
Ni-5-300-B			88,000		1.55		68	
Ni-5-400-A	400	77,000		1.60		63		
Ni-5-400-B			80,000		2.35		65	
Ni-5-500-A	500	69,000		1.60		73		
Ni-5-500-B			71,000		2.35		76	
Ni-5-600-A	600	58,000		1.60		68		Argon
Ni-5-600-B			62,000		1.60		68	atmosphere
Ni-5-700-A	700	18,000		13.0		47		
Ni-5-700-B			22,000		21.5		50	
Ni-5-800-A	800	11,000		18.00		48		
Ni-5-800-C			13,000		18.00		43	

long path of rupture, has been increased by the lowering of the temperature to −185° C. In sample Ni-3, which has been deformed at room temperature only two-thirds as much as Ni-1, may be seen the direct effect of this deformation factor. The decrease in the amount of amorphous reinforcement has lowered the maximum tensile strength from 158,000 to 148,000 lb. per sq. in. By increasing the temperature of deformation, but maintaining it below the annealing temperature, the tensile strength is further decreased. Ni-5, Fig. 21, was subjected to the same amount of working as Ni-3, but at a higher temperature (400° C.). Copper[2] and molybdenum behave in the same manner. On the other hand, iron, when deformed at 400° C., exhibits an increased tensile strength when tested between room temperature and 600° C. At liquid-air temperatures this effect apparently disappears.[2] The increase in tensile strength thus produced in iron may be attributed to the allotropic transformation at about 400° C. Deformation in the range of increased tensile

[2] Jeffries: *Op. cit.*

TABLE 6.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-1) Swaged and Drawn Hot (1300° — 1000° C.) from 0.125 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-1-L-A	−185	212,000		0.00		0.00		
Mo-1-L-B		208,000		0.00		0.00		
Mo-1-R-A	25	148,000		4.70		68		
Mo-1-R-B			153,000		5.49		68	
Mo-1-100-A	100	131,000		1.55		71		
Mo-1-100-B			133,000		3.15		75	
Mo-1-200-A	200	120,000		0.80		75		
Mo-1-200-B			120,000		0.80		75	
Mo-1-300-A	300	104,000		0.80		79		
Mo-1-300-B			108,000		0.80		83	
Mo-1-400-A	400	100,000		0.80		87		
Mo-1-400-B			102,000		0.80		87	
Mo-1-500-A	500	98,000		<0.5		89		
Mo-1-500-B			100,000		<0.5		87	
Mo-1-600-A	600	96,000		<0.5		88		Argon
Mo-1-600-B			98,000		<0.5		88	atmosphere
Mo-1-700-A	700	88,000		<0.5		89		
Mo-1-700-B			90,000		<0.5		90	
Mo-1-900-A			78,000		<0.5		88	

strength might well increase the strength of the metal at other temperatures.

The curve for annealed nickel (Ni-2), Fig. 20, shows a decided discontinuity between 250° and 350° C., when the fall in tensile strength ceases. This is slightly lower than the temperature usually given for the loss of magnetic properties in nickel; as shown by the elongation-temperature curve, Fig. 22, there is a transformation range of at least 100°. In the case of iron, the increase in tensile strength at 200° C. is as much as 25 per cent. Nickel shows no such increase, hence it is not surprising that the nickel deformed at 400° C. does not gain in strength at lower temperatures, as does the iron.

Reduction of Area of Nickel Wire

Fig. 24 shows the reduction of area of annealed and cold-worked nickel throughout the temperature range employed. Both curves seem

TABLE 7.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-2) Swaged and Drawn (800° C. — Black Heat) from 0.125 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-2-R-A	25	154,000		5.70		65		
Mo-2-R-D			156,000		6.10		65	
Mo-2-100-C	100	144,000		1.55		68		
Mo-2-100-D			149,000		2.35		70	
Mo-2-200-A	200	137,000		0.80		70		
Mo-2-200-B			140,000		0.80		73	
Mo-2-300-A	300	130,000		0.80		79		
Mo-2-300-B			132,000		0.80		79	
Mo-2-400-A	400	125,000		0.80		79		
Mo-2-400-B			127,000		0.80		80	
Mo-2-500-A	500	117,000		<0.5		83		
Mo-2-500-B			117,000		<0.5		85	
Mo-2-600-A	600	111,000		<0.5		85		Argon atmosphere
Mo-2-600-B			112,000		<0.5		87	
Mo-2-700-A	700	107,000		<0.5		87		
Mo-2-700-B			109,000		<0.5		87	
Mo-2-900-A	900	94,000		<0.5		90		

to be governed by some modification acting between 100° and 500° C. The general trend, however, shows increased reduction as the temperature rises from — 185° to 600° C. The peak of Ni-1 at 700° C. should be attributed to a fine-grained structure at the lowest temperature of annealing. As the temperature increases, the resulting coarser grain developed opposes a high reduction at the point of fracture. Also the annealed sample attains its greatest reduction of area in the temperature range corresponding to the rise in elongation.

The temperature of the transformation point in nickel is apparently determined by the impurities present. In a recently published paper,[3] Browne and Thompson in describing the physical properties of nickel cite nine values with the chemical analysis for each. They range from 340° C. for the purest nickel to 310° C. in the case of a 95 per cent. nickel. Our present conception that allotropy occurs only in crystalline material is borne out by the behavior of the nickel wires under consideration. The

[3] D. H. Browne and J. F. Thompson: Physical Properties of Nickel. *Bull.* 153 (Sept., 1919).

TABLE 8.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-3) Swaged and Drawn Hot (1300° — 1000° C.) from 0.045 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-3-L-A	−185	140,000		0.00		0.00		
Mo-3-L-B			140,000		0.00		0.00	
Mo-3-R-A	25	115,000		9.50		58		
Mo-3-R-C			119,000		11.00		58	
Mo-3-100-A	100	105,000		6.30		64		
Mo-3-100-B			110,000		9.40		64	
Mo-3-200-A	200	95,000		2.30		70		
Mo-3-200-B			98,000		4.50		73	
Mo-3-300-A	300	92,000		0.80		79		
Mo-3-300-B			95,000		0.80		82	
Mo-3-400-A	400	86,000		0.80		82		
Mo-3-400-B			90,000		0.80		84	
Mo-3-500-A	500	82,000		<0.5		86		
Mo-3-500-B			82,000		<0.5		84	
Mo-3-600 A	600	80,000		<0.5		88		Argon atmosphere
Mo-3-600-B			81,000		<0.5		88	
Mo-3-700-A	700	75,000		<0.5		90		
Mo-3-700-B			77,000		<0.5		88	
Mo-3-900-A	900	65,000		<0.5				

variations in both tensile strength and elongation in the critical temperature range are most apparent in the case of the annealed nickel.

Elongation of Nickel Wire

Indications of an allotrope in nickel are much more strikingly shown by the elongation curve for annealed nickel (Ni-2), Fig. 22. The elongation falls normally as the temperature rises from 25° to 200° C., when a change appears to set in resulting in increased elongation over a range of about 300° reaching the maximum at 500° C. As the temperature rises above 500° C., the curve falls until recrystallization sets in between 600° and 700° C.

At liquid-air temperatures, there is a slight drop in ductility in annealed nickel (Ni-2). This sample, as shown in Fig. 5, possesses a fairly large grain size, which fact would indicate a decrease in ductility at −185° C.; in this respect it is analogous to iron.[4]

[4] Jeffries: *Op. cit.*

TABLE 9.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-4) Swaged and Drawn (800° C. — Black Heat) from 0.045 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-4-L-A	−185	145,000		0.00		0.00		
Mo-4-L-B		143,000		0.00		0.00		
Mo-4-R-A	25		121,000		6.25		53	
Mo-4-R-C		115,000		6.25		50		
Mo-4-100-C	100		108,000		5.90		56	
Mo-4-100-D		104,000		3.20.		50		
Mo-4-200-A	200	96,000		0.80		73		
Mo-4-200-B			98,000		0.80		70	
Mo-4-300-A	300	95,000		<0.5		75		
Mo-4-300-B			97,000		0.80		77	
Mo-4-400-A	400	95,000		<0.5		81		
Mo-4-400-B			95,000		<0.5		81	
Mo-4-500-A	500	89,000		<0.5		85		
Mo-4-500-B			90,000		<0.5		85	
Mo-4-600-A	600	85,000		<0.5		88		Argon
Mo-4-600-B			87,000		<0.5		88	atmosphere
Mo-4-700-A	700	87,000		<0.5		89		
Mo-4-700-B			87,000		<0.5		90	

Of the three samples of worked nickel, Ni-1, which was worked the most, as shown in Fig. 22, increases in ductility down to the lowest temperature of test; the increase is less in Ni-3, Fig. 23, and Ni-5. In fact, Ni-5, which was deformed at 400° C., seems to have its maximum elongation at a temperature slightly above that of liquid air.

All of the worked samples become less ductile as the temperature rises to 300° C., but the force that is so manifest in the annealed nickel between 200° and 500° shows itself. Even those samples of which the behavior, because of previous working, is controlled by the amorphous phase, slightly regain their ductility at 300° and 400° C. This is first effected in Ni-3 and Ni-5 in which the crystalline material suffered the least rearrangement. Between 600° and 700° annealing sets in, causing a rapid rise in ductility, which continues up to 1000° C. Fig. 6 shows the microstructure of Ni-1 after the tensile test at 700° C. The small grain size explains the rapid rise in the elongation curve between 600° and 700° C. Price and Davidson[5] give 650° C. as the temperature of rapid soften-

[5] This volume, 415.

TABLE 10.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-5) Annealed to give Medium Grain Size*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-5-L-A	−185	96,000		0.00		0		
Mo-5-L-B		89,000		0.00		0		
Mo-5-R-A	25	63,000		0.00		0		
Mo-5-R-C			63,000		0.00		0	
Mo-5-100-A	100	59,000		9.00		0[a]		
Mo-5-100-B		61,000		5.30		0		
Mo-5-200-A	200	58,000		12.50		0[a]		
Mo-5-200-B			58,000		10.50		0	
Mo-5-300-A	300	49,000		22.50		55		[b]
Mo-5-300-B			53,000		20.50		40	
Mo-5-400-A	400	49,000		7.00		45		
Mo-5-400-B			52,000		8.60		50	
Mo-5-500-A	500	49,000		4.70		50		[c]
Mo-5-500-B			51,000		7.80		65	[d]
Mo-5-600-A	600	50,000		7.80		68		Argon
Mo-5-600-B		51,000		6.00			70	atmosphere
Mo-5-700-A	700	51,000		7.00		73		
Mo-5-700-B		51,000		6.20			73	
Mo-5-900-A	900	48,000		2.10				
Mo-5-900-B			50,000		6.20			
Mo-5-C-A	−50	83,000		0.00		0		

[a] Slight local reductions not at fracture.
[b] Fracture largely transcrystalline.
[c] Necking more regular in outline than at 400°.
[d] Necking extends over considerable length.

ing and fall in tensile strength of nickel. Fig. 6 should be compared with their Fig. 3, which shows nickel annealed at 650° C. after 73 per cent. reduction by rolling.

From 750° to 1050° C., the decrease in scleroscope hardness is from 9.5 to 6.5. The elongation of Ni-1 increases over this same temperature range from 16 to about 25 per cent. The grain size developed during the application of load at 1000° C. in the case of Ni-2 is extremely large (see Fig. 7). The constant application of load and continuous deformation above 700° C. is doubtless responsible for this rapid grain growth. Its effects will be observed most in the decrease in area reduction above 700° C., Fig. 24.

TABLE 11.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-6) Annealed to give Extremely Small Grain Size*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-6-L-A	−185	152,000		0.80		0		
Mo-6-L-B		149,000		0.00		0		
Mo-6-C-A	−50	151,000		11.00		55		
Mo-6-C-B		149,000		12.50				
Mo-6-R-A	25	125,000		20.00		66		
Mo-6-R-B			129,000		22.60		70	
Mo-6-100-A	100	114,000		17.30		68		
Mo-6-100-B			117,000		22.00		70	
Mo-6-200-A	200	105,000		14.00		78		
Mo-6-200-B			106,000		19.50		78	
M0-6-300-A	300	95,000		9.40		85		
Mo-6-300-B			97,000		10.20		85	
Mo-6-400-A	400	88,000		7.00		86		
Mo-6-400-B			90,000		8.00		88	
Mo-6-500-A	500	80,000		6.25		89		
Mo-6-500-B			82,000		6.25		90	
Mo-6-600-A	600	79,000		2.35		90		Argon
Mo-6-600-B			79,000		3.90		90	atmosphere
Mo-6-700-A	700	76,500		2.35		93		
Mo-6-700-B			77,500		3.15		93	
Mo-6-900-A	900	71,000		1.80		93		

MECHANICAL PROPERTIES OF MOLYBDENUM WIRES

The samples of molybdenum were prepared to furnish evidence of the influence of degree and temperature of working. It was desired especially to ascertain the influence of grain size in a metal of the class of molybdenum and tungsten. The temperatures of test are well below that of equal cohesion for molybdenum. In the scale of metals this metal holds a position between tungsten and those metals represented by nickel and iron. The behavior of tungsten, as reported by Jeffries, will be often used as a basis of comparison in the following discussion.

Tensile Strength of Molybdenum Wire

Unlike tungsten, molybdenum does not decrease in tensile strength between room and liquid-air temperatures. The combined influence of

TABLE 12.—*Mechanical Properties at Various Temperatures of Molybdenum Wire (Mo-7) Treated to Develop Extremely Large Grains*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Mo-7-L-A.	−185	102,000		0.00		0		
Mo-7-L-B		93,000		0.00		0		
Mo-7-R-A	25	42,500		3.15		0		
Mo-7-R-B			42,500		3.15		0	
Mo-7-100-A	100	36,000		3.90		0		
Mo-7-100-B		34,000		4.70			0	
Mo-7-200-A	200	28,000		8.70		0		*
Mo-7-200-B			28,000		7.50		0	
Mo-7-300-A	300	31,000		10.20		100		"Wedge" at
Mo-7-300-B			33,000		11.00		100	fracture
Mo-7-400-A	400	27,500		6.25		100		
Mo-7-400-B			28,500		10.10		100	
Mo-7-500-A	500	27,000		3.10		100		
Mo-7-500-B			28,000		3.90		100	
Mo-7-600-A	600	28,000		2.35		100		Argon
Mo-7-600-B			29,000		3.90		100	atmosphere
Mo-7-700-A	700	30,000		3.15		100		
Mo-7-700-B		30,000		3.15			100	
Mo-7-900-A	900	29,500		3.10		100		

* Local reductions not at fracture.

heavy working and low temperatures produces a maximum tensile strength of 210,000 lb. per sq. in. in Mo-1 at −185° C.; see Fig. 25. Mo-1 and Mo-2 were both reduced 96 per cent. by working, but Mo-1 was worked at a temperature about 400° above Mo-2; the colder worked is the stronger in all cases.

Mo-3 and Mo-4, both reduced 70 per cent. by working, developed only about 75 per cent. of the maximum strength of the more severely worked metal. As before the hotter worked is the weaker at all temperatures of test. Mo-5, Mo-6, and Mo-7 are the annealed wires of different grain size. Figs. 9, 10, and 11 illustrate their respective structures. Mo-6, which has the smallest grain, is the strongest at all temperatures. The others are of about the same strength at −185° C. but the tensile strength of the wire with the largest grain size falls at room temperature to about two-thirds that of the wire with the intermediate grain size. Between 1000° and 900° C., however, the

TABLE 13.—*Mechanical Properties at Various Temperatures of Aluminum Wire (Al-1) Drawn Cold from 0.090 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Al-1-L-A	−185	64,000		5.00		26		
Al-1-L-B		62,000		7.00		30		
Al-1-C-A	− 50	49,000		3.10				
Al-1-C-B			51,000		3.90		38	
Al-1-C-C			50,000		4.30		30	
Al-1-R-A	25	49,000		1.06		25		
Al-1-R-B		50,000		3.00		40		
Al-1-R-C			52,000		4.70		38	
Al-1-R-D			51,000		3.90		25	
Al-1-R-F		49,000		1.55				
Al-1-100-A	100	42,000		0.80		20		
Al-1-100-B			46,000		1.55		35	
Al-1-100-C		44,000		1.55		30		
Al-1-200-A	200	26,500		6.25		56		a
Al-1-200-B			29,000		4.00		50	
Al-1-200-E		27,000		6.80				
Al-1-240-A	240	17,500		10.90		62		b
Al-1-240-B			26,500		5.50		62	
Al-1-300-A	300	17,300		7.60		68		
Al-1-300-B			21,500		3.10		60	
Al-1-400-A	400	16,000		9.40		80		
Al-1-400-B			20,000		7.80		80	
Al-1-500-A	500	6,100		12.00		92		
Al-1-500-B			5,500		28.00		98	
Al-1-630-A	630		500		6.00		0.00	

[a] Registered load fell to 16,000 during 1 min. of pull.
[b] Registered load fell to 13,000 during 1 min. of pull.

tensile strengths of the two samples of coarser grain remain practically constant. The few points that lie off the curves must be due to some slight and unavoidable variation in grain size between specimens. This flatness in the tensile-strength curve shows how slightly the crystalline phase decreases in tensile strength as the temperature rises. The tensile strength above 900° C. should not drop suddenly until the temperature approaches the melting point. Tensile strength is a complex property, while the elastic limit is the measure of cohesion. The elastic limit probably decreases more rapidly than the tensile strength with rise in temperature. The curve for Mo-7, Fig. 25, shows the tensile strength of molybdenum composed almost completely of the crystalline phase.

TABLE 14.—*Mechanical Properties at Various Temperatures of Aluminum Wire (Al-2) Annealed at 400° C. for 15 Min.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Al-2-L-B	−185	41,000		18.50		44		
Al-2-2-D			41,000		34.00		58	
Al-2-R-A	25	29,500		16.50		65		
Al-2-R-B		29,500		20.00		60		
Al-2-R-C			29,000		14.00		70	
Al-2-R-D			29,000		20.00		70	
Al-2-R-G		28,000		16.50				
Al-2-R-H			28,500		14.00			
Al-2-100-A	100	26,500		18.50		64		
Al-2-100-B			27,500		18.75		69	
Al-2-100-C		28,000		18.75				
Al-2-200-A	200	18,000		25.00		69		
Al-2-200-B			22,000		16.40		69	
Al-2-200-C		17,500		24.10				
Al-2-200-E			20,000		20.00			
Al-2-300-A	300	16,300		12.50		90		A and D
Al-2-300-D			16,500		17.00		84	in furnace
Al-2-300-C		8,500		24.00		95		1 min.
Al-2-300-B			10,000		24.00		84	B and C in furnace 5 min.
Al-2-400-A	400	12,000		17.00		91		
Al-2-400-B			11,500		19.00		95	
Al-2-500-A	500	5,000		19.00		84		
Al-2-500-B			6,000		20.00		96	
Al-2-600-A	600		3,500	17.00		94		
Al-2-600-B		3,000			17.00		94	
Al-2-630-A	630		1,000		1.55		0	
Al-2-630-B			500		0.00		0	
Al-2-630-C			500		0.00		0	
Al-2-620-A	620	1,000		12.5		0		
Al-2-620-B			1,000		15.50		84	Long reduction

NOTE.—All reductions of area above 300° extend over some length, with exception of those above 600° C. as marked.

Elongation of Molybdenum Wires

In their behavior as regards ductility, molybdenum and tungsten approach each other. At liquid-air temperatures, elongation in both is lacking; from their comparative elongations at room temperature, however it may be assumed that molybdenum will retain its ductility at a lower temperature than tungsten.

TABLE 15.—*Mechanical Properties at Various Temperatures of Aluminum Wire (Al-3) Drawn Cold from 0.040 to 0.025 In.*

Test Mark	Temp., Degrees C.	Tensile Strength, Pounds per Square Inch		Elongation, Per Cent. in 2 In.		Reduction of Area, Per Cent.		Remarks
		Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	Slow Loading	Rapid Loading	
Al-3-L-A	−185	59,000		7.80		35		
Al-3 L-B			59,000		5.60			
Al-3-R-B	25	51,000		3.12		52		
Al-3-R-D			51,000		3.12		52	
Al-3-100-B	100	45,000		2.35		50		
Al-3-100 D			46,500		3.12		52	
Al-3-200-A	200	27,000		7.50		63		
Al-3-200-B			31,000		3.15		60	
Al-3-240-A	240	20,000		10.20		73		
Al-3-240-B			28,000		8.60		70	
Al-3-300-A	300	16,000		7.00		73		
Al-3-300-C			17,000		10.10		75	
Al-3-400-A	400	13,000		9.40		85		
Al-3-400-B			17,000		8.60		88	
Al-3-500-A	500	4,700		26.5		95		
Al-3-500-B			5,600		16.5			

Mo-1, the most severely worked sample, at room temperature has an elongation of 5 per cent.; Mo-3 and Mo-4, which were less severely worked, possess greater elongation at this temperature. Of these two the hotter worked wire shows the higher ductility, the same as copper and nickel. Tungsten, after an equal amount of deformation, breaks with no elongation at room temperature; after a deformation equal to that of Mo-1, tungsten shows a 6 per cent. elongation at room temperature.

After a 70 per cent. reduction, tungsten is brittle at room temperature; molybdenum shows an elongation of from 7 to 10 per cent. The tungsten, however, has a maximum of 12 per cent. elongation at 200° C. A 93 per cent. deformation reduces the maximum elongation at any temperature of both tungsten and molybdenum, but at the same time it imparts to the metal the ability to retain ductility at lower temperatures. On this basis the direction of the elongation curves has been determined in Fig. 28; the elongation curves for annealed molybdenum wires are shown in Fig. 27. These curves show the relation between the grain size and the elongation throughout the temperature range studied.

Mo-6, the average diameter of the grain of which is 0.0002 in., attains its maximum elongation at room temperature; the elongation

Mo-6 resembles closely a heavily worked wire; see Fig. 29. At −50° C. its reduction in area at fracture is 55 per cent., while its elongation is about 10 per cent. Both of these properties are the result of a large number of crystalline units bound together by a fine network of amorphous material. The crystalline phase can be deformed by sufficient load, which is transmitted through the amorphous cement. At lower temperatures, the elastic limit or resistance to deformation of the crystalline phase has so increased that before any deformation begins rupture occurs along the grain boundaries. The path of rupture, while shorter than in the case of Mo-1, is much more intricate than in the two samples of coarser grain. A comparison of their respective tensile strengths at −185° C. will emphasize this fact.

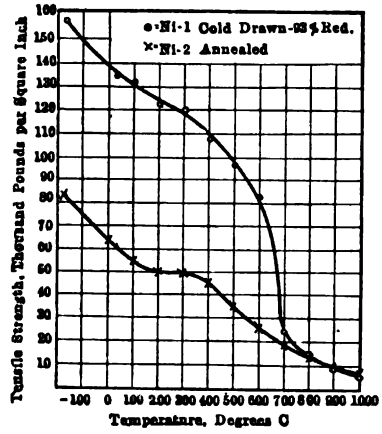


FIG. 20.

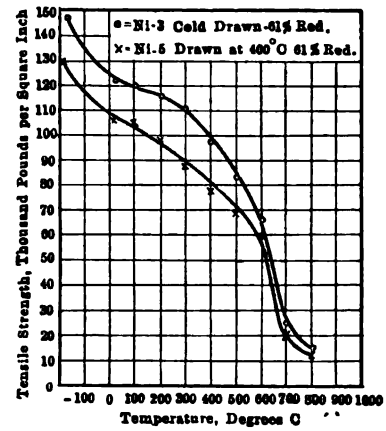


FIG. 21.

FIGS. 20 AND 21.—TENSILE STRENGTH-TEMPERATURE CURVES FOR NICKEL WIRES

Mo-5, the wire having the intermediate grain size, first shows a reduction at about 200° C., but the necking increases up to 800°, where it tends to assume a constant value, though one considerably lower than the smaller grain size; see Fig. 29. The fracture is decidedly intercrystalline below 100° C. but, at 300°, passes through the grains which have been distorted by the load. The change in the position of the fracture in the wire of large grain size (Mo-7) is marked by a sudden rise in the curve representing the per cent. reduction of area. At 200° C., the wire breaks at the grain boundary; at 300° C. it breaks through the grain. Above 300°, as far as the tests were carried, the fracture remained transcrystalline. The reduction of area above 300° took the shape of a wedge having 100 per cent. reduction in one plane and no reduction in the plane at right angles to the first; Fig. 12 shows two views of this fracture, Fig. 17 shows the form of fracture more clearly. Many of the grains in the region of the fracture showed this directional reduction in one plane while the

diameter at the grain boundary remained unreduced. This surface effect was easily noticeable with the naked eye and a longitudinal section of such a wire is shown in Fig. 19.

In an aggregate of grains under tension each grain tends to reduce in cross-section 100 per cent. in one plane and none at all in the plane at right angles to the first. Because of difference in orientation, the reduction tendencies of adjoining grains will tend to counteract each other. Consequently, the greater the number of grains in a cross-section the greater will be the total reduction at the point of fracture, but the reduction in such an aggregate will always be less than in a cross-section composed of a single grain. The effect of orientation opposing the reduction in adjoining grains is illustrated in Fig. 19. Here the greatest reduction

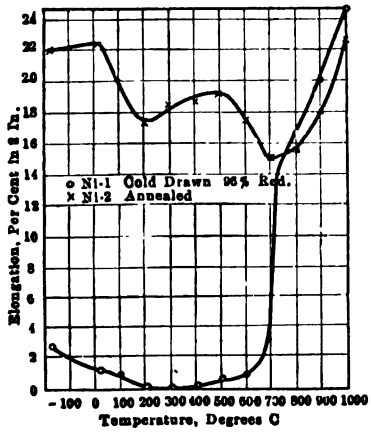


FIG. 22.

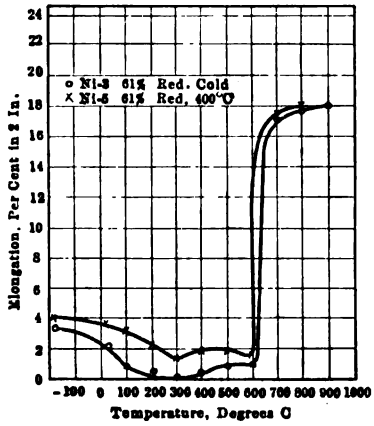


FIG. 23.

FIGS. 22 AND 23.—ELONGATION-TEMPERATURE CURVES FOR NICKEL WIRE.

occurred in the middle of the grains while the grain boundary has suffered no reduction. Here also is an illustration of the shift in path of rupture caused by a slight change in temperature.

This same intercrystalline brittleness is apparent in equiaxed tungsten up to 200° C. In tungsten, as small a grain as that in Mo-6 would have no elongation at room temperature. Jeffries attributed this brittleness to internal stress due to a difference in the coefficients of expansion of the crystalline and amorphous phases. The same explanation will cover the behavior of molybdenum, though the stress is developed at lower temperatures in the latter case.

The tensile-strength curves of molybdenum have been extended downward, by dotted lines, below liquid-air temperatures, in Fig. 25. This fall in strength might be expected to occur at some temperature slightly lower than −185° on the basis of the fall in tensile strength of tungsten between 25° C. and −185° C.[6]

[6] Jeffries: *Op. cit.*

Mechanical Properties of Aluminum-copper Alloy

The aluminum-copper samples furnish an alloy of the solid-solution type. Because the solubility of $CuAl_2$ varies with the temperature, the properties of this alloy at all temperatures might be expected to differ somewhat from those of the pure metals. Pure aluminum melts at 658° C. and the 3 per cent. of copper lowers the melting point to about 648° C.

Tensile Strength of Aluminum Wires

The tensile-strength curves in Figs. 31 and 32 show a drop from liquid-air temperatures to near the melting point in the worked and annealed samples. A slight flattening of the curve seems to occur through about

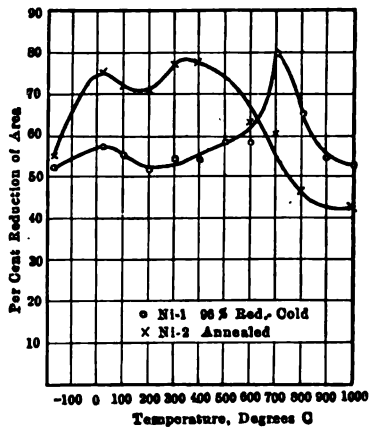


Fig. 24.—Reduction of area-temperature curves for nickel wires.

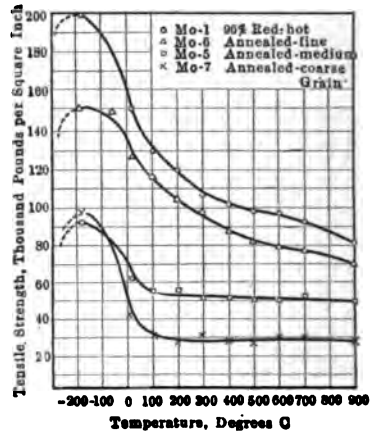


Fig. 25.—Tensile strength-temperature curves for molybdenum wires.

100° near room temperature. A suggestion of this same feature will be found in the tensile-strength curves for worked copper occurring at about 150° to 250° C.[7] Whether or not such action is to be considered a general rule in all metals near their equicohesive temperature is yet to be determined; with iron and nickel the effects of allotropy may mask this discontinuity in the curves.

The degree of deformation has made little difference in the tensile strengths at room temperature, though at −185° the sample reduced 93 per cent. (Al-1) begins to show an increase in strength over Al-3, which was reduced 61 per cent. Al-4, which was reduced 61 per cent. at 175° C., is almost identical with Al-3, which was reduced the same amount at room temperature; even at liquid-air temperature the tensile strength of the two may be considered equal, perhaps the usual differences might develop as the temperature fell still lower. The constant difference in

[7] Jeffries: *Op. cit.*

tensile strength and elongation between the two annealed wires (Al-2 and Al-7) may be ascribed to a probable contrast in grain size. In the case of each sample, the tensile strength drops very rapidly between 100° and 200° C.

Elongation of Aluminum Wires

The elongation curves, Fig. 33, of the annealed wires show an enormous fall from −185° C. to room temperature, when they begin to rise. The rate of loading above 100° C. has a decided bearing on the elongation values, and even at room temperature these fail to check consistently.

The elongation drops rapidly at 630° C. The specimens that determined this point on the curve were loaded merely by the weight of the

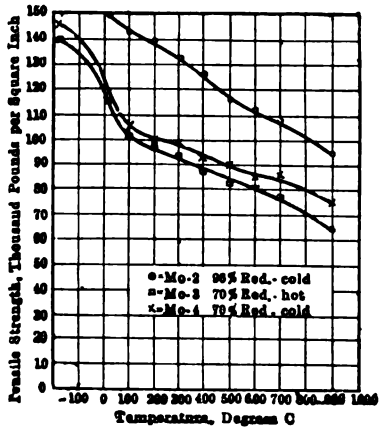


FIG. 26.—TENSILE STRENGTH-TEMPERATURE CURVES FOR MOLYBDENUM WIRES.

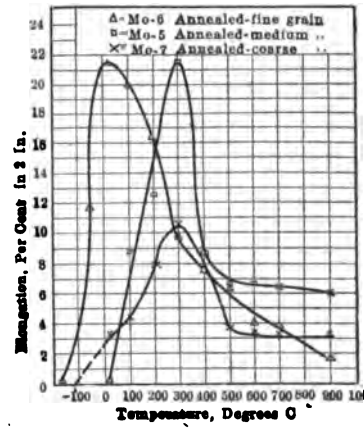


FIG. 27.—ELONGATION-TEMPERATURE CURVES FOR MOLYBDENUM WIRES.

lower jaw and its fitting and suspended in the furnace at a temperature of about 550° C. The temperature was slowly raised until fracture occurred with no elongation and no reduction of area. The only concrete evidence of intercrystalline fracture is given in Fig. 16 which shows the two ends of the fracture. From the evidence submitted by Rosenhain and Ewen,[8] it is safe to assume that this fracture is intercrystalline.

In contrast to the annealed wires, those that have been reduced by working fall in elongation from −185° C. to 100° C. and then rise steadily up to 500° C. This rise in elongation takes place in both the annealed and cold-worked samples of the alloy. It begins first in the annealed wire and, at 100° higher, in the cold-worked. In this respect the

[8] Walter Rosenhain and Donald Ewen: Intercrystalline Cohesion in Metals *Jnl.* Inst. Metals (1912) **8**, 149.

alloy behaves in a similar manner to nickel and iron. In all three cases the rise in elongation is most pronounced in the annealed samples. A decided drop in elongation at 630° is also noticed in the case of Al-1, though the loading was made in the usual continuous manner and undoubtedly some deformation took place before the wire had attained the temperature indicated.

Reduction of Area of Aluminum Wires

Following the general type of such curves the reduction of area rises continuously from −185° to near the melting point; see Fig. 34. The discontinuity in the tensile-strength curves near room temperature is also evident here. In the case of Al-2, the rapid rise in reduction between 200° and 300° C. indicates definite annealing temperature in this range.

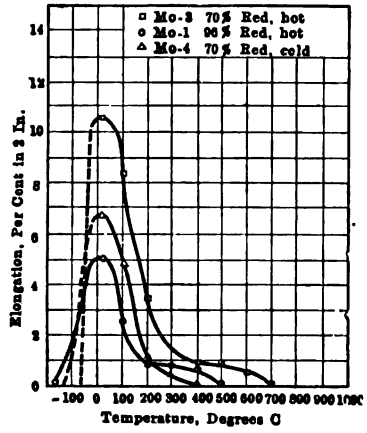


FIG. 28.—ELONGATION-TEMPERATURE CURVES FOR MOLYBDENUM WIRES.

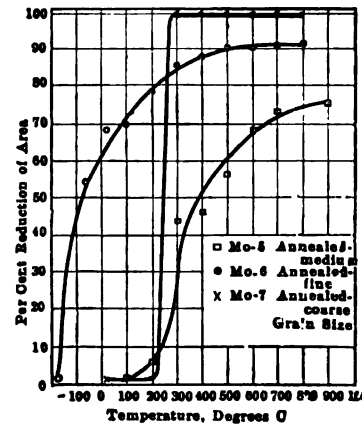


FIG. 29.—REDUCTION OF AREA-TEMPERATURE CURVES FOR MOLYBDENUM WIRES.

Huntington,[9] in his report on tensile tests of pure aluminum between room temperatures and 650° C., described a sudden drop to zero in both elongation and reduction curves at the melting point. The same action occurred in this case. On the other hand the elongations of his specimens of rolled aluminum begin to increase at room temperature, without the drop to 100° that is shown in Fig. 33.

The features displayed by the material used in these tests may well be ascribed to the action of the copper content of the alloy. Moreover, we are working with a metal close to its equicohesive temperature, which cannot be far from 200° C.

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[9]A. K. Huntington: Effect of Temperature on Tensile Tests of Copper and its Alloys. *Jnl.* Inst. Metals (1912) **8**, 126.

Effect of Variation in Rate of Loading Upon Elongation and Tensile Strength

It is generally conceded that tensile strength and elongation may be considerably influenced by the rate at which the load is applied to the test piece. The scheme followed throughout this series of tests and the form of record submitted were adopted with a view to determining the extent of this factor.

In Fig. 37 are plotted, for Ni-2, the elongation values at each temperature for the two rates of loading employed. The increase in elongation accompanying rapid loading is less noticeable at the lower temperatures but grows as the temperature rises and reaches a maximum

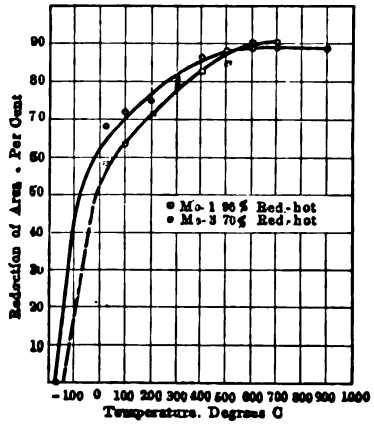

Fig. 30.—Reduction of area-temperature curves for molybdenum wires.

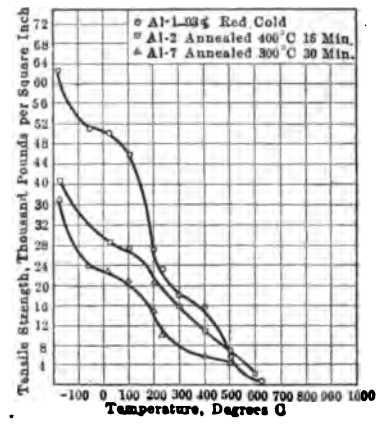

Fig. 31.—Tensile strength-temperature curves for aluminum-copper alloy.

at 900° C., about 200° above the lowest temperature of recrystallization. The temperature range where the element of time assumes such importance that the slowly loaded wire stretches considerably more than that loaded eight times as rapidly should be noted. This range might be safely assigned a value of 150° C. and within it lies the actual temperature of recrystallization.

The maximum reduction of area in worked nickel occurs at the same temperature as the increased elongation by slow loading. Identical features mark the curves thus plotted for the worked alloy, Fig. 35. The difference in favor of rapid loading at room temperature disappears below 200°; between 200° and 400°, greater elongation occurs with slow loading but at 500° the rapidly loaded specimen stretches 28 per cent., which is more than twice as much as that loaded slowly.

Fig. 36 shows the difference in tensile strength due to different loading rates in Al-1. Rapid loading results in higher values for tensile

strength at all temperatures below 500° C.; the greatest difference is apparent between 200° and 400°, corresponding to the range noted in the elongation curves. Tables 13 to 17 show that this effect of loading rate upon tensile strength is more noticeable in the worked samples than in the annealed.

In Fig. 38, an attempt is made to illustrate the behavior of the test specimens. The curve marked Al-1-200-A represents the gradual increase in registered stress up to the maximum in about 20 sec. of loading. With a constant rate of loading, the stress slowly falls for 40 sec. until fracture occurs at about 60 per cent. of the maximum load. By increasing the rate of loading eight times, the registered stress reaches a maxi-

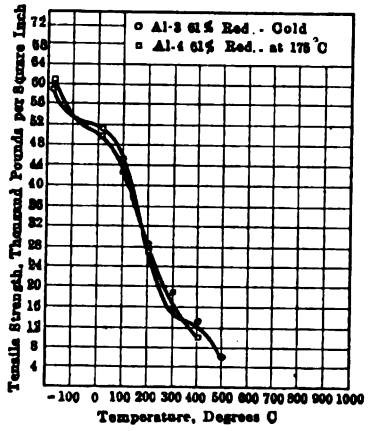

FIG. 32.—TENSILE STRENGTH-TEMPERATURE CURVES FOR ALUMINUM-COPPER ALLOY.

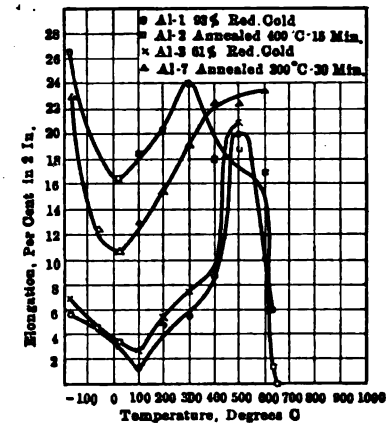

FIG. 33.—ELONGATION-TEMPERATURE CURVES FOR ALUMINUM-COPPER ALLOY.

mum in about 5 sec. and gradually falls off through 10 sec., fracture occurring at a stress 10 per cent. below the maximum.

At 600° C., this flowing of the metal under stress gives rise to a time-stress curve Al-2-600-A. The rise is more gradual, consuming 60 sec., while the fall requires 80 sec. The piece fractures at 17 per cent. of the maximum load of the test piece.

The results are an elongation of 17 per cent. or more in some cases and a 95 per cent. reduction of area. The reduction extends over a considerable length and is represented in Fig. 15. Bengough[10] says "The unstable vitreous amorphous material of Beilby's plays a far more fundamental part in determining the mechanical properties of metals and alloys than has hitherto been suspected" and again "In some cases the mechanical properties of metals at high temperatures could be best explained by the

[10]G. D. Bengough: Discussion on Intercrystalline Cohesion in Metals. *Jnl.* Inst. Metals (1912) 8, 180.

authors' (Rosenhain and Ewen) view that the cement persisted up to high temperatures in the neighborhood of the melting point. For instance a certain brass pulled out to a fine point, just like glass would do. In other cases, especially with cast metals, this did not happen at all; the elongation was low and numerous cracks developed at varying distances from the point of fracture."

The behavior of zinc in tensile tests between room temperature and 200° C. has been described by Mathewson, Trewin, and Finkeldey,[11] who reproduce (from Martens) the stress-deformation curve for zinc tested at room temperature. They state that "permanent set increases after each stage of loading even in the case of very small loads." There is a

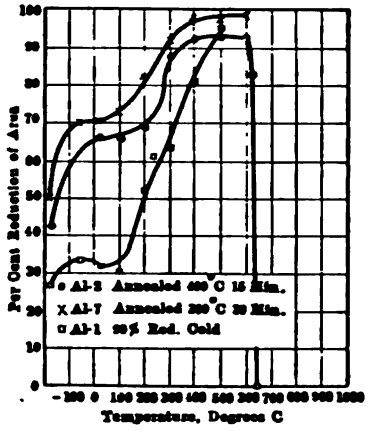

FIG. 34.—REDUCTION OF AREA-TEMPERATURE CURVES FOR ALUMINUM-COPPER ALLOY.

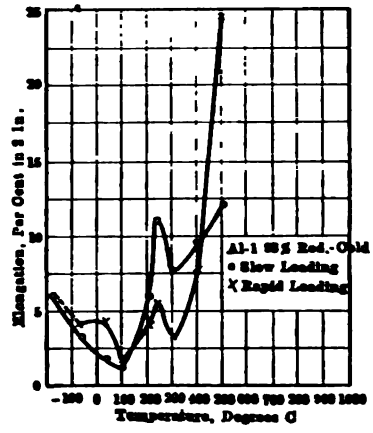

FIG. 35.—VARIATION IN ELONGATION WITH CHANGE IN RATE OF LOADING, ALUMINUM-COPPER ALLOY.

rapid decrease in load as the time of test progresses, the load at the end of 10 min. having fallen to 70 per cent. of the maximum stress registered.

Thus zinc in tension at room temperatures exhibits features noticeable in the aluminum-copper alloy at about 200° C. The curves show that the tensile strength of zinc declines rapidly at room temperature; the flattening of this curve sets in at about 100° C. It might be predicted that the tensile-strength curve would continue to rise steeply as far as −100° C. before changing its rate of increase. The elongation of zinc seems to increase, in general, as the temperature rises above 25° C. (the lowest temperature studied). Above 150° C., the elongation drops, as does that of aluminum under steadily applied load above 500° C. Aluminum and zinc furnish excellent examples from which to judge of the properties of metals in the vicinity of their equicohesive temperatures or the range just below and including their "annealing" temperatures.

[11] C. H. Mathewson, C. S. Trewin, and W. H. Finkeldey: Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod. This volume, 305.

General Considerations

According to Bengough[12] the elongation curve for copper falls abruptly from a high value at 900° C. to zero at 1050°. A fracture the same nature as the intercrystalline fracture of aluminum at 630° C. seems to have occurred. The curve, though, shows an inflection between 800° and 900° C., which the author is not able to explain; this no doubt is due to a variable rate of loading. In regions of rapid grain growth, much above the annealing temperature, the rate of loading will so seriously disturb the uniformity of elongation figures as to practically prohibit the drawing of a single curve in this region. Jeffries[13] has shown a range in elongation

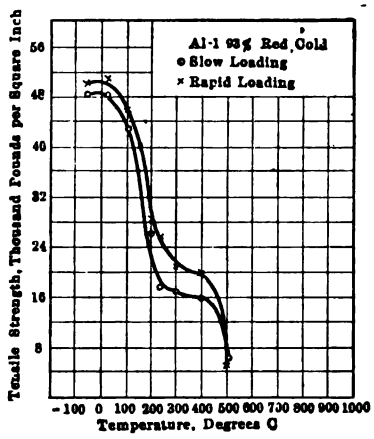

FIG. 36.—VARIATION IN TENSILE STRENGTH WITH CHANGE IN RATE OF LOADING, ALUMINUM-COPPER ALLOY.

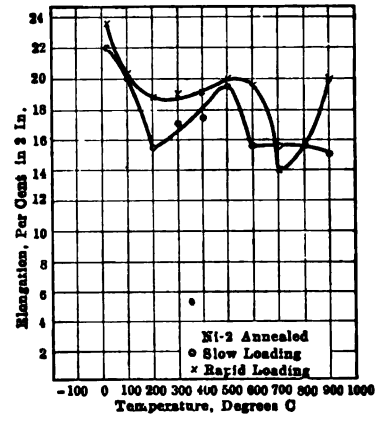

FIG. 37.—CURVES SHOWING RELATION BETWEEN ELONGATION AND RATE OF LOADING AT VARIOUS TEMPERATURES.

due to difference in loading rates and grain size that meets the conditions existing in higher temperature ranges.

Some curves plotted by Huntington[14] for a copper-nickel alloy, showing tensile strength, elongation, and reduction between room temperature and 500° C., exhibit discontinuities at about 430° C. The values for each of these properties increase at this temperature, though the curves are drawn to omit the actual values. This range happens to be near the critical temperature for the transformation in nickel and the seeming irregularities in the curves mentioned may well be attributed to the 15 per cent. of the nickel in the alloy.

Bengough applies the term "temperature of recuperation" to the temperature above which the decrease in tensile strength becomes less

[12] G. D. Bengough: A Study of the Properties of Alloys at High Temperatures. *Jnl.* Inst. Metals (1912) 7.

[13] *Op. cit.*

[14] *Op. cit.*

rapid with rising temperature; that is, the tensile-strength curve flattens decidedly. It is stated that above this temperature worked and annealed metal have the same tensile strength, while below it the worked metal is the stronger. At temperatures above that of "recuperation" the metal resembles a viscous liquid of very low strength and great ductility. It is described, also, as "the lowest temperature at which it is

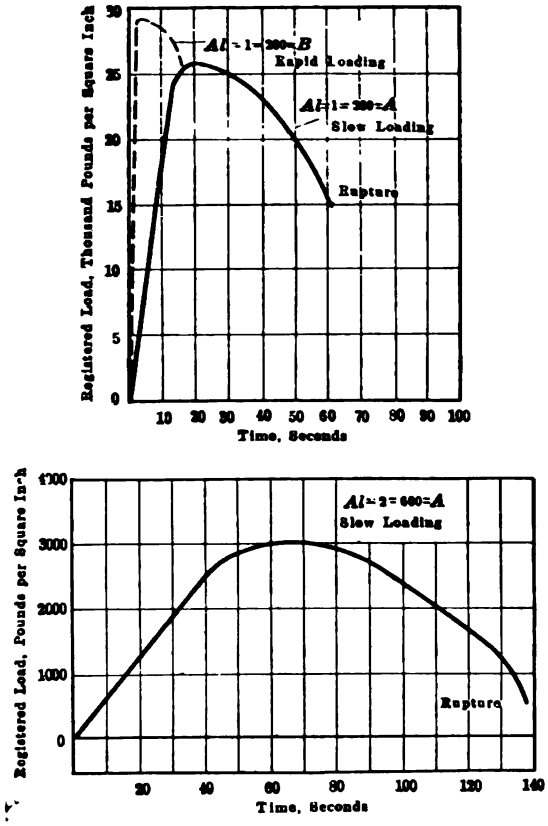

FIG. 38.

possible to harden a metal by working." The diagram given by Bengough seems to place the "temperature of recuperation" considerably above the actual annealing temperature, so that his last definition is not strictly in accord with his curves.

The gradual decrease in tensile strength above the annealing temperature is explained by the tensile-strength curves of the coarse-grained specimens of molybdenum, Fig. 25. In these samples, the tensile strength does not decrease appreciably over a range of 800° C.

When a metal is deformed continuously above its annealing temperature, the amorphous metal generated at once recrystallizes. During this

cycle the metal under load will elongate through flow of the amorphous as well as deformation of the crystalline material. At a temperature well above that of annealing, rapid loading augments this combined flow and deformation and results in high elongation.

Conclusions

Evidence has been produced to establish the types of curves that represent variation in tensile strength, elongation, and reduction of area with variation in temperatures for all metals. These basic curves are subject to variations produced by any allotropic change that may take place in the metal under consideration.

Excluding allotropic changes and other specific characteristics, all metals possess the same fundamental properties and those exhibited by any one metal are functions of the temperature at which the observations are made.

The maximum reduction of area by fracture in tension occurs in a piece of metal in which single grains occupy the entire cross-section. In the case of two aggregates, the one of smaller grain size suffers the greater reduction.

The ultimate result of decreasing temperature is a complete loss of ductility and probably eventually a reduction in tensile strength. Brittleness is first observed in metals having equiaxed structures. The smaller the grain size of a sample the lower is the temperature to which ductility is preserved.

Deformation of a metal below its annealing temperature makes its maximum ductility at any temperature below that of working less than that of the same metal in the unworked condition. But the worked sample will retain its power of elongation to a lower temperature.

DISCUSSION

Zay Jeffries, Cleveland, Ohio.—The results of six metals, especially when the variety of the metals tested is considered, gives much more conclusive evidence regarding generalities than the results on three. The metals now given these general tests are tungsten, iron, copper, molybdenum, nickel, and aluminum. The crystal structures involved represent the two main types, with tungsten, molybdenum, and iron as body centered cubic; and copper, nickel, and aluminum as face centered cubic.

Lead, copper, aluminum, platinum, gold, silver, and nickel crystallize in the face-centered cubic lattice. It is characteristic of these metals that they hold their ductilities to very low temperatures. All of these metals are ductile in liquid air when annealed. The body-centered metals become brittle at a higher temperature on cooling than the face-

centered. Tungsten and molybdenum are entirely brittle in liquid air; iron, as ordinarily produced, in the annealed condition is brittle in liquid air. One specimen of nearly pure iron had about 11 per cent. elongation, in liquid air; it had been annealed at such a temperature as to be very fine grained. Mr. E. C. Bain and I have found that manganese steel is face-centered cubic but iron at room temperature is body-centered. Hadfield has observed that manganese steel is very ductile in liquid air, which bears out the general conclusion that the face-centered metals retain their ductilities at lower temperatures than the body-centered.

Another generality that can be drawn from these tests is that whether the metal is face-centered or body-centered, working at a certain temperature below the recrystallization point and testing at a still lower temperature increases ductility. That action is not a function of the crystal structure but a function of plastic deformation.

Although we have not studied specifically the effect of change of temperature on hexagonal metals, like zinc and magnesium, these metals harden at a faster rate during deformation than the cubic metals.

Another generality that seems to hold pretty well is that the rate of change of physical properties of metals with changing temperature is somewhat a function of the weight of the atom. The rate of change of aluminum and magnesium is quite large; these metals have light atoms. The rate of change in metals with heavy atoms, such as gold, platinum, and lead, is small. That generality should hold owing to the mechanism of the atomic motion as related to temperature itself.

W. H. Bassett, Waterbury, Conn.—Will you explain a little further the face-centered and body-centered cubic crystallization?

Zay Jeffries.—In the body-centered lattice, the elementary cube consists of an atom at each corner and an atom in the center of the cube. In the face-centered lattice, the elementary cubic unit consists of an atom at each corner and an atom in the center of each face of the cube, and these structures repeat throughout the mass of any one crystal. Both structures are in the isometric or the cubic system; in mineralogy the face-centered corresponds most nearly to the octohedral structure.

F. E. Carter.—The composition of the nickel is given as 99.8; is that nickel plus cobalt?

W. P. Sykes.—Yes; no attempt was made to analyze the cobalt, but it was about 0.5 per cent.

Treatment Tests on Ores of Consolidated Coppermines Co.

By Robert Linton,* New York, N. Y.

(New York Meeting, February, 1921)

In 1898, Joseph L. Giroux and J. A. Snedaker organized the Pilot Knob Copper Co. and began developing the Pilot Knob mine at Kimberly, Nev., for high-grade copper ores, carrying good gold and silver values, that the formation had disclosed. At that time the nearest railroad was over 150 mi. distant. The high-grade ores did not prove to be extensive at this point—at least to the depth (240 ft.) to which the work was carried—but development of neighboring claims indicated extensive deposits of sulfide porphyry ore of concentrating grade lying at shallow depth, and deeper deposits of direct-smelting oxidized ores occurring in limestone near the limestone-porphyry contact. The properties passed through the hands of several organizations, with only meager development, until acquired in 1913 by Consolidated Coppermines Co., whose holdings now comprise 3480 acres of mining claims in the Robinson district. Since that time development has been prosecuted more actively; and for the purpose of determining the most efficient and economical method of treating the ores, considerable testing work has been done during the past three years, both in the laboratory and in actual mill operations.

At first, the shipments were of ore high enough in grade to be profitable even with the long wagon hauls to the railroad and prevailing freight and smelting charges. In 1905, a blast furnace and a concentrator were erected at Kimberly. On account of insufficient ore supply, the blast furnace was never blown in and later was dismantled. The concentrator as originally equipped was operated for only about two months, both because the ore supply at that time was not sufficient and because gravity concentration did not yield satisfactory extraction. The location and arrangement of the mill further entailed high operating costs.

In 1908, the Nevada Consolidated Copper Co. began to mill successfully, on a large scale, its sulfide porphyry ores, which are similar in character to the adjacent Coppermines ores. After that time, all of the ores and concentrates produced by Coppermines Company were smelted and a considerable part of the Coppermines low-grade ores concentrated at the Steptoe works of the Nevada Consolidated Co.

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* Vice President and Managing Director, Consolidated Coppermines Co.

No records of production prior to 1906 are available, but the amount was very small. From 1906 to 1911 inclusive, returns from sales of ore amounted to $35,590.35. In 1912, shipments of ore to the Steptoe Reduction Works was commenced and production of copper since then has been as follows:

	Pounds Copper		Pounds Copper
1912	3,768,521	1916	973,248
1913	6,550,088	1917	9,801,252
1914	1,742,979	1918	15,768,481
1915	1,803,366	1919	3,897,934

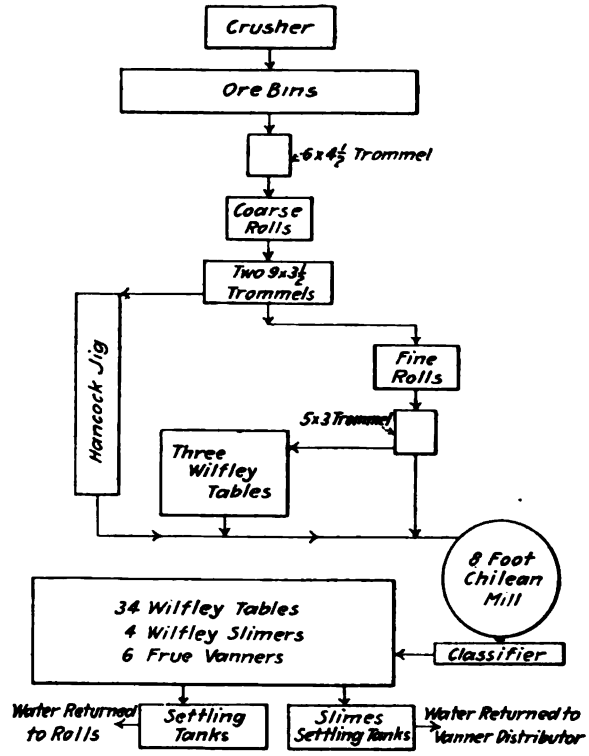

FIG. 1.—FLOW SHEET OF OLD CONCENTRATOR.

RESULTS OBTAINED WITH FIRST CONCENTRATOR

The old concentrator, which was put into operation in November, 1908, and operated about two months, produced concentrates that were sold for $26,570.09. No details of the mill run are on record. The mill followed the lines for water concentration in general use at that time; the flow sheet was about as shown in Fig. 1.

Results of Water Concentration

From 1912 to 1919, considerable tonnages of porphyry ore from the Coppermines properties were concentrated at the Steptoe works, in which operation water concentration was used exclusively. A summary of the results is given in Table 1.

TABLE 1.—*Summary of Results of Water Concentration*

	1912	1913	1914	1915	1916	1917	1918	1919
Grade of ore, per cent..	1.975	1.73	1.49	1.59	1.54	1.355	1.545	1.385
Grade of concentrates..		12.50	10.20	10.60	10.20	8.21	9.84	10.28
Ratio of concentration.		11.7:1	10.76:1	10.22:1	10.20:1	10.12:1	10.02:1	11.88:1
Copper recovery, per cent.....	71.1	65.7	59.30	61.60	60.00	59.86	64.00	62.49

DETAILS OF RESULTS FOR YEAR 1919

Dry tons ore concentrated.....	80013	Grade of ore.....	1.385
Dry tons concentrates produced	6735	Grade of concentrates.....	10.278
Ratio of concentration.....	11.88 into 1	Grade of tailings.....	0.567
Degree of concentration.....	7.42 into 1	Per cent. recovery.....	62.49

ANALYSES

	ORE	CONCENTRATES		ORE	CONCENTRATES
Cu, per cent.....	1.376	10.14	CaO, per cent.....	0.7	1.2
SiO_2, per cent.....	63.6	26.6	S, per cent.....	2.7	23.2
Al_2O_3, per cent....	11.8	6.8	Au, oz.....	0.011	0.083
Fe, per cent.....	5.0	23.9	Ag, oz.....	0.045	0.222

These results probably represent the best that could be done with water concentration.

CLASSIFICATION AND COMPOSITION OF ORES

Three classes of copper ores have been developed on the Kimberly properties:

1. Disseminated sulfides in porphyry occurring in large continuous masses, which can be mined at low cost either by underground methods or by steam shovel from open pits. The copper is in the form of chalcocite with some associated pyrite.

2. Heavy sulfide ore, in which the copper occurs chiefly as chalcopyrite, with considerably higher pyrite contents. The ore lies in porphyry on or near the limestone porphyry contact. In the Old Glory mine, developed ore averages 3.21 per cent. copper. In the Taylor mine, little development work has been done, but there is promise of a considerable tonnage of ore that will average around 3 per cent. copper and $2 of gold and silver. Churn drilling and underground development in the vicinity of the Old Glory mine indicate quite an additional tonnage of high-sulfur ore of lower copper contents.

3. Oxidized ores in limestones, occurring as replacements along or near the limestone-porphyry contact. These ores have been developed only in the Alpha mine, where they occupy a leached and altered zone that has been developed for a maximum length of about 1000 ft. (304 m.) and a maximum width of about 500 ft., in which the oxidized ores have been followed by underground workings and diamond drilling from the 800-ft. level to 1550 ft. below the collar of the shaft. The copper minerals are chiefly cuprite, chalcocite, and melaconite, with some admixture of azurite, malachite, and native copper. The orebodies are irregular in size and shape and lie along much larger limonitic masses, which carry small or fractional percentages of copper. There have been mined and shipped from the Alpha mine about 90,000 tons of ore that average 7.42 per cent. copper. In addition quite a tonnage of oxidized porphyry ores overlies the sulfides; besides, there are in the Alpha mine oxidized ores lower than smelting grade. No plan for treating these lower grade oxidized ores has as yet been worked out. Analyses of the ores mined and treated are given in Tables 2 and 3.

TABLE 2.—*Composition of Disseminated Porphyry Ore*

	1914	1915	1916	1917	1918		1919	
					Ora	Morris Brooks	Ora	Morris Brooks
Cu, per cent.....	1.554	1.594	1.593	1.135	1.545	1.217	1.376	1.441
SiO_2, per cent....	66.0	64.0	64.0	64.5	67.2	86.9	63.6	85.0
Al_2O_3, per cent...	12.9	13.4	13.6	13.5	12.3	1.7	11.8	3.6
Fe, per cent.....	4.2	4.6	4.7	4.8	3.9	3.5	5.0	3.8
CaO, per cent....	1.2	1.6	1.0	1.5	1.1	2.3	0.7	2.4
S, per cent.....	2.1	2.6	2.7	3.1	2.9	2.0	2.7	3.2
Au, oz.....	0.016	0.017	0.013	0.012	0.018	0.018	0.01	0.02
Ag, oz.....	0.032	0.046	0.039	0.041	0.057	0.062	0.05	0.08

TABLE 3.—*Composition of Direct Smelting Oxidized Ore, Alpha Mine*

	1917	1918	1919
Cu, per cent.....	8.88	7.26	7.8
SiO_2, per cent.....	41.80	36.00	34.90
Al_2O_3, per cent.....	15.55	23.60	21.70
Fe, per cent.....	13.30	10.40	12.40
CaO, per cent.....	1.40	1.40	0.80
S, per cent.....	0.50	0.41	0.30
Au, ounce.....	0.005	0.005	0.0004
Ag, ounce.....	0.11	0.13	0.008

Neither the Old Glory nor the Taylor ores have, as yet, been mined in quantity, but sampling indicates the composition shown in Table 4.

TABLE 4.—*Composition of Old Glory and Taylor Ores*

	Old Glory	Taylor First Class	Taylor Second Class
Cu, per cent	3.2	5.0	3.0
Insoluble, per cent	58.0	55.0	63.0
Fe, per cent	18.0	13.0	7.0
S, per cent	9.6	12.0	6.0
Au, oz	1.5	0.08	0.06
Ag, oz		1.5	0.60

REMODELED MILL AND RESULTS OBTAINED

In the summer of 1916, the General Engineering Co., of Salt Lake City, Utah, was engaged to make tests on the porphyry sulfide ores to determine their adaptability to flotation. These tests, which were made with the Callow pneumatic flotation machine, satisfied the General Engineering Co. that the ore was entirely amenable to flotation; so it recommended that the mill be remodeled in accordance with the results obtained. A summary of the tests is as follows:

1. 974 gm. of the ore was ground in a ball mill to pass 48-mesh, 2 lb. per ton of oil being added. The oil mixture used was: General Engineering Co., No. 89, 50 per cent.; No. 78, 25 per cent.; No. 2, 25 per cent. The pulp was then treated in a Callow cell and the flotation tailings retreated on a small Wilfley table, with the following results:

	TOTAL COPPER	OXIDIZED COPPER
Heads by assay, per cent	1.41	0.107
Heads calculated from products, per cent	1.48	0.114
Flotation concentrates, per cent	16.10	0.18
Flotation tailings, per cent	0.348	0.109
Table concentrates, per cent	3.79	0.26
Table tailings, per cent	0.294	0.107
Combined concentrates, per cent	14.05	0.193
Final tailings, per cent	0.294	0.107
Ratio of concentration	11.6 into 1	
Recovery, total, per cent	81.86	
Recovery, oxides, per cent	14.51	

2. 978 gm. of the ore was ground in a ball-mill to pass 48-mesh, with sodium sulfide added at the rate of 4 lb. per ton, and the same proportion and mixture of oils used in the first test. As before, the pulp was treated in a Callow cell and the flotation tailings retreated on a Wilfley table; the results were as follows:

	Total Copper	Oxidized Copper
Heads by assay, per cent	1.41	0.107
Heads calculated from products, per cent	1.48	0.116
Flotation concentrates, per cent	12.57	0.18
Flotation tailings, per cent	0.246	0.109
Table concentrates, per cent	4.65	0.29
Table tailings, per cent	0.20	0.107
Combined concentrates, per cent	11.90	0.19
Final tailings, per cent	0.20	0.107
Ratio of concentration	9.14 into 1	
Recovery, total, per cent	87.95	
Recovery, oxides, per cent	17.85	

In December, 1916, additional tests were run on a second lot of ore, which assayed 2.74 per cent. total copper, 0.315 per cent. oxidized copper. The ore was crushed to 48 mesh with a mixture of equal parts of coal-tar creosote and light Pensacola pine oil. The screen analysis was as follows:

	Per Cent.		Per Cent.
Through 35 mesh	100.00	Retained on 150	16.46
Retained on 48	5.88	Retained on 200	11.76
Retained on 65	13.72	Through 200	41.71
Retained on 100	10.97		

Five tests were run, treating the pulp in a Callow cell and retreating the tailings on a Wilfley table, with the following results:

	1	2	3	4	5
Copper assay flotation concentrates, per cent	11.94	20.41	18.30	19.57	21.15
Copper assay table concentrates, per cent	22.83	21.78	20.93	26.40	20.36
Copper assay combined concentrates, per cent	14.36	20.71	18.88	21.08	20.97
Copper assay tailings, per cent	0.79	0.66	0.63	0.58	0.60
Recovery copper, per cent	74.89	78.14	79.31	80.81	79.90

The oil varied from 5 lb. per ton in the first test to 2½ lb. in the last. The five tests are figured from five sets of concentrate and tailing samples taken at intervals of approximately 1 hr. during mill run. The final tests showed the following results. Heads, 2.70 per cent. (0.315 oxides); tailings, 0.73 per cent.; ratio of concentration, 9.67 into 1; recovery, total, per cent., 75.83. The analysis of concentrates was: copper, 19.8 per cent.; iron, 18.58 per cent.; insoluble, 35.11 per cent.

In line with these tests, the concentrator was remodeled to use pneumatic oil flotation, followed by retreatment of flotation tails on

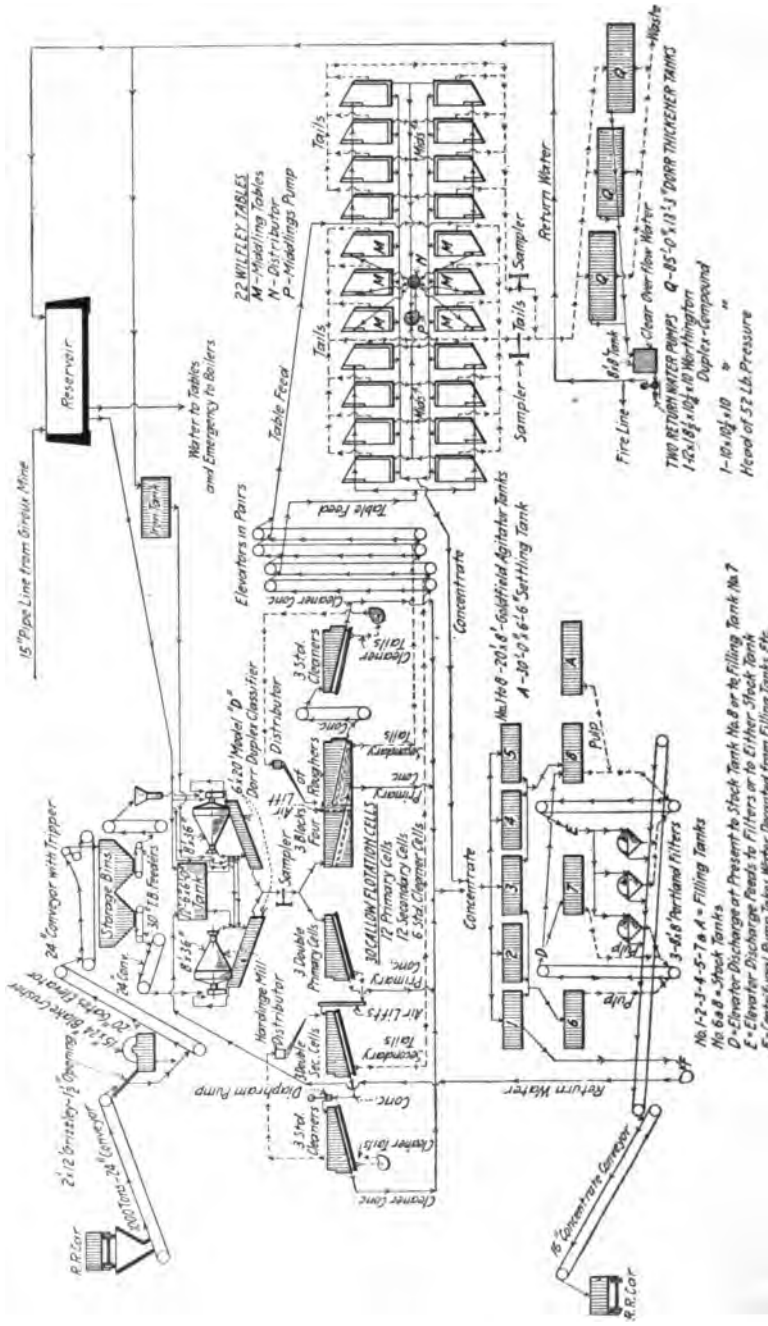

FIG. 2.—FLOW SHEET, 1000-TON FLOTATION AND CONCENTRATION PLANT.

Wilfley tables. Its capacity was 500 tons per day at first, but later it was increased to 1000 tons per day; the flow sheet is shown in Fig. 2. Two runs were made: the first from February to December, 1917; the second from March, 1918 to January, 1919. There were treated as follows:

Year	Tons ore	Grade Per Cent.	Copper produced Pounds
1917	144,204	1.69	3,320,727
1918	246,417	1.23	4,528,774
1919	17,552	1.44	471,605
Total	408,173	1.44	8,321,106

From the time when the mill was started in February, 1917, to August, 1918, various combinations of coal tar, coal-tar creosote, No. 80 Pensacola pine oil, and No. 4 Barrett light flotation oil were employed, with lime to maintain the circuit alkaline. The details of the operations are shown in Table 5.

TABLE 5.—*Details of Mill Operations, February, 1917 to August, 1918*

	Ratio of Concentration	Pounds Oils Used per Ton Ore				Lb. Lime per Ton Ore	Proportion of Flotation Concentrates, Per Cent.	Copper Assay of Concentrates Per Cent.	Mill Recovery, Per Cent.	Per Cent. on 48 Mesh	Pulp Density
		Coal Tar	Coal Tar Creosote	No. 80	No. 4						
1917											
May	12.4:1	1.39	0.09	0.027	0.12	2.39	76.8	13.80	60.7	5.20	2.76
June	10.0:1	1.36	0.16	0.17	0.055	3.40	30.0	12.32	70.1	4.64	3.18
July	10.2:1	1.49	0.28	0.21	0.032	2.36	72.5	13.52	71.0	4.25	3.22
August	10.0:1	1.62	0.24	0.21		2.59	72.4	15.50	78.7	4.92	3.29
September	10.4:1	1.65	0.28	0.26		3.36	76.1	18.42	83.9	4.33	3.07
October	11.4:1	1.44	0.21	0.18		3.77	78.1	15.40	82.2	4.50	3.00
November	13.4:1	1.25	0.16	0.16		3.16	72.2	15.20	75.6	3.60	3.10
December	12.1:1	1.26	0.15	0.08		3.58	70.5	15.10	77.4	3.30	3.00
1918											
March	15.0:1	1.18	0.13	0.10		3.26	74.6	15.20	73.5	3.29	2.9
April	13.2:1	1.33	0.15	0.15		3.52	62.4	11.30	65.8	3.8	3.0
May	17.7:1	0.95	0.18	0.05		2.58	56.3	13.10	72.8	4.7	3.0
June	13.7:1	1.09	0.35	0.03		1.38	64.1	17.00	84.8	5.7	3.3
July	21.6:1	1.10	0.27			1.85	55.0	17.30	75.3	7.4	3.0
August	20.4:1	1.17	0.28			1.63	54.7	20.18	75.0	6.1	3.15

It will thus be seen that the results of operation were fully up to that indicated by the preliminary tests of the General Engineering Co., when the difference of the grade of the ore is taken into consideration.

In the summer of 1918, Mr. J. M. Callow, President of the General Engineering Co., suggested to the writer the use of the patented "X-Y

Reagents," which reagents — X-cake (alpha + beta naphthylamine) and xylidin (nitrol)—were being successfully used as a substitute for flotation oils. Accordingly the use of this treatment was begun on Sept. 1, 1918. There was a marked increase in the recovery of sulfides, both of copper and of iron, and a corresponding decrease in the silica and alumina contents. The moisture of the concentrates coming off the filters was reduced almost one half. The use of the reagents was continued until the mill was closed down. Table 6 shows the details of operations during this period.

TABLE 6.—*Details of Mill Operations, September, 1918 to January, 1919*

	Ratio of Concentration	Reagents Used, Pounds per Ton		Lime	Prop. of Flotation Conc.	Copper Assay of Conc.	Mill Recovery	Per cent. on 48 mesh	Pulp Density
		X-Cake	Xylidin						
Sept.....	21.2:1	0.225	0.115	1.58	77.9	18.0	79.3	5.5	3.37
Oct.....	21.1:1	0.129	0.08	1.87	77.6	20.65	83.3	5.33	3.42
Nov.....	19.6:1	0.121	0.082	2.52	78.8	20.06	81.5	5.4	3.40
Dec.....	17.5:1	0.13	0.076	2.99	74.8	18.85	78.0	7.28	3.40
Jan.....	18.7:1	0.155	0.99	2.82	79.8	21.0	86.2	6.85	3.55

For comparison, the results in 1918 with oils and with X-Y reagents are as follows:

COAL-TAR REAGENTS

	Copper, Per Cent.	Gold, Oz.	Silver, Oz.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	Iron, Per Cent.	CaO, Per Cent.	Sulfur, Per Cent.
Analysis mill heads.....	1.186	0.018	0.059	87.1	1.5	3.5	2.1	2.1
Analysis mill tails.....	0.277	0.009	0.039	91.5	1.1	2.2	2.2	0.5
Analysis concentrates.....	13.623	0.140	0.329	27.3	7.2	20.9	1.3	22.9
Recoveries.....	78.22	52.95	38.11	2.14	32.81	40.84	4.24	75.65

Ratio of concentration, 14.68 into 1; per cent. of H_2O in concentrate, 17.15; cost of flotation reagents per ton milled, 7.46 cents.

X-CAKE AND XYLIDIN

	Copper, Per Cent.	Gold, Oz.	Silver, Oz.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	Iron, Per Cent.	CaO, Per Cent.	Sulfur, Per Cent.
Analysis mill heads.....	1.336	0.019	0.07	85.9	2.5	3.7	2.5	2.5
Analysis mill tails.....	0.206	0.006	0.04	90.1	2.3	2.1	2.6	0.5
Analysis concentrates.....	18.33	0.210	0.436	13.5	4.5	27.6	0.3	32.1
Recoveries.....	82.31	69.30	40.34	0.97	12.02	46.61	0.64	80.79

Ratio of concentration, 19.00 into 1; per cent. of H_2O in concentrate, 9.39; cost flotation reagents per ton ore milled, 15.6 cents.

Notwithstanding the considerably higher cost per ton of X-Y reagents,

an actual per ton saving was made by their adoption for the reason that a higher ratio of concentration was obtained and consequently a higher grade of concentrate. This reacted in favor of lower costs, as follows: First, a smaller tonnage of concentrate was handled in the mill (filtered, etc.). Second, a smaller tonnage of concentrate was treated by the smelter, cutting freight and treatment charges per ton almost in two. Third, the higher grade of concentrate was made largely by the elimination of colloidal matter, giving a more granular product. This, combined with the smaller tonnage to be handled, made it possible to filter the concentrate in one shift with one or two filters, whereas with the old concentrate, produced with coal-tar reagents, three shifts with three filters were necessary to handle the concentrate produced. Fourth, owing to the more granular nature of the concentrate, as compared with that produced with coal-tar reagents, a thicker, dryer cake was produced by the filters, thus saving freight on moisture.

Tests of Ore in Minerals Separation Machine

In the spring of 1918, Mr. Frederick Laist, of Anaconda, Mont., was called into consultation on the metallurgy of the Coppermines ores. Under his direction, a series of tests was run in an outside testing plant, using a Minerals Separation type of apparatus. The complete analysis of the ore, which was a 10-ton lot shipped from the Morris-Brooks mine, is given in Table 7.

Table 7.—*Analysis of Ore from Morris-Brooks Mine*

Cu, total, per cent.. 1.29	Zn..... Trace	Insoluble, per cent.. 84.4
Cu, oxide, per cent.. 0.03	FeO, per cent... 6.6	Al_2O_3, per cent..... 9.8
Ag, oz. per ton..... 0.10	S, per cent..... 2.7	As_2O_3, per cent..... 0.21
Au, per cent..... Trace	CaO, per cent.. 1.7	Sb_2O_3, per cent..... Trace
Pb, per cent..... Trace	MgO, per cent. 1.3	Mn, per cent..... nil

Tests of this ore were run in July and August, 1918, and again in April and May, 1919. Oxidation had been going on in the ore, which had been lying exposed to the weather, so that the proportion of copper as oxide had risen from 0.03 to 0.18 per cent. Probably for this reason the recoveries in 1919 were not quite as high as in 1918, when the tests were made on fresh ore. Four tests were run in 1918 and eight in 1919, using from 762 to 1497 lb. of ore. In 1918, the pulp was floated in a twelve-cell Minerals Separation machine used as a rougher and the concentrates cleaned in a single-cell machine. During the winter of 1918–19, the twelve-cell machine was arranged so that three cells could be used as cleaners; the 1919 tests were run in this modified machine, with the further object of determining whether or not the working temperature could be reduced, which had been indicated in the first tests. It was found that by using a combination of 65 per cent. coal tar, 30 per cent. crude pine oil, and 5 per cent. steam-distilled pine oil, good results were obtained down to 55° F. Slightly better results were obtained at 75° F.

DISCUSSION

J. M. CALLOW, Salt Lake City, Utah (written discussion).—In addition to the marked superiority of the X-Y reagents over oils in the recovery of copper and the grade of the concentrates that Mr. Linton has pointed out, the tables on page 824 show a greater recovery of the gold and (to a lesser extent) silver. Raising the recoveries from 78.22 to 82.31 per cent. and the concentrates from 13.62 to 18.33 per cent. copper, reducing the combined silica and alumina from 34.15 to 18 per cent. and the moisture in the concentrates from 14.68 to 9.39 per cent. are all positive accomplishments shown by the tables, but a result that the tabulations cannot show is the much greater ease and the smaller skill required to produce a better and more uniform result than can be obtained with oils.

X-cake is crude alpha-naphthylamine and Y (liquid) is crude xylidin. The letters are used for simplicity. X-cake is the flotation agent and xylidin is used as a solvent. The standard X-Y mixture, made up of 60 per cent. crude alpha-naphthylamine and 40 per cent. crude xylidin, is shipped in drums or tank cars. It is added to the flotation feed in the same manner as the usual flotation oils, except that it may be added at the flotation cells instead of in the grinding mills.

The remarkable difference in the filtering rate and the percentage of moisture in the filtered concentrate is explained by the property of the X-Y reagents to float less of the slimy and colloidal gangue. Concentrates made by these reagents will settle much faster and give a much thicker filter feed, varying from 65 to 70 per cent. solids. It is, therefore, possible to introduce the table concentrates with the flotation product without experiencing any difficulty in the operation of the filters on account of this coarser material settling in the bottom of the filter tanks. With this mixture of products at Coppermines, even where producing a filter cake from 2 to 3 in. thick, the moisture content still remained below 10 per cent.

In regard to the tests made by Mr. Laist in a Minerals Separation machine with oils, from which the conclusion is drawn that a concentrate could probably be made carrying 20 to 25 per cent. insoluble, a tailing carrying 0.15 per cent. copper, and a recovery of 88 per cent., two important factors must have been assumed: First, that the ore would not become oxidized after breaking in the mine and, second, that the clean ore from the orebody proper would not become mixed with the capping from the oxidized zone; as a matter of fact both of these occurred during the whole of the mill-operating period mentioned.

It must also have been assumed that the continued use of approximately 0.4 lb. of pine oil in a closed alkaline circuit (where the tailings discharge is maintained at thicker than 50 per cent. solids) would not bring about complications. In practical operations with Coppermines'

mine water, it was found that a much smaller quantity of pine oil did interfere, and that the results improved as the quantity of pine oil was reduced to a minimum. The amount of pine oil used was gradually reduced to 0.03 lb. per ton and finally discontinued entirely. It is to be presumed that these tests were conducted with ordinary city water. The mine water and that used in the Salt Lake City laboratory were so different that oils that gave good results in Salt Lake City failed completely when used at the plant. Test-plant results can be duplicated in practice only when all the test-plant conditions are duplicated in practice, and vice versa.

If the results given in Tables 8 and 9 are taken in conjunction with the fourth conclusion at the end of the paper, the impression is gained that violent agitation gives better results than the pneumatic machines. To this and to the remarks regarding the experiments with pneumatic machines at the testing plant, the writer takes exception.

The 1918 results with oils and pneumatic flotation in the mill compare very favorably with the testing-plant results, without making any allowance for the difference in conditions, especially as to crushing and heat and the interference to flotation due to capping in the mill ore. These comparisons are made additionally plain by Table 10.

TABLE 10

	PER CENT. ON 48 MESH	PER CENT. OF COPPER RECOVERED	PER CENT. OF COPPER IN CONCENTRATES
Average of eight testing-plant tests, Table 9.	3.4	82.2	16.7
Mill results, Sept., 1918 to Jan., 1919, X-Y reagents	6.07	82.31	20.7
Mill results, 1918, with oils	5.17	78.22	13.62

Steel Chimneys and their Linings in Copper Smelting Plants

By A. G. McGregor, Warren, Ariz.

(New York Meeting, February, 1921)

In the Southwest a number of large steel chimneys discharge the gases from the copper smelting furnaces. Some of these chimneys show no deterioration after twenty years, others show serious deterioration after four years service.

A steel stack 20 ft. 7½ in. (6.3 m.) in diameter by 279 ft. (85 m.) high, Fig. 1, used for roaster gases only at the Calumet & Arizona Mining Co.'s plant at Douglas, Ariz., was lined to the top of the bell, 40 ft. (12 m.) from the base, with common brick placed on end, lime and cement mortar being used. Above the bell, the stack was lined with 4 by 4 by 8 in. (10 by 10 by 20 cm.) building tile, placed on end, making a lining 4 in. thick. The tiles were supported on angle-iron rings, riveted to the inside of the chimney shell about 15 ft. apart.

The chimney was put into use in the latter part of 1913. Four years later, considerable of the tile lining had fallen out of place and mixed with the flue dust at the bottom of the chimney. About a year later, several flattened and distorted sheets were noticed about 70 ft. below the top. An investigation showed that the thickness of these distorted sheets, which was originally ¼ in., had been reduced one half. One year later, or six years after the chimney went into use, several holes, a square foot and smaller in area, appeared near the flat spots mentioned. Soon afterwards, when the chimney was shut down for repairs, it was found that most of the tile lining for 125 ft. from the top had fallen out and that the steel shell was badly corroded; but where the lining remained in place the shell was undamaged. Many of the tile which had fallen out of place had become soft or flaky and crumbling, others were as hard as when placed. An analysis of the hard and soft tile is shown on p. 2. These tile were of a fireclay mixture, and were used instead of common brick on account of lower cost.

The steel forming the upper 125 ft. (38 m.) was replaced, and a 4¼-in. (11-cm.) lining of firebrick was laid from the bell to the top of the chimney. The brick were placed on end, wedges and keys being used. After each 8-in. course was set, keyed, and wedged tight, thin mortar —water, sodium silicate, and finely ground silica—was worked into the joints. The brick are supported on angle-iron rings, every 15 ft., in the same way as the tile.

ANALYSIS OF TILE LINING IN ROASTER CHIMNEY

	HARD TILE, PER CENT.	SOFT AND CRUMBLING TILE, PER CENT.
Silica, SiO_2	66.1	69.5
Alumina, Al_2O_3	22.9	18.1
Ferric oxide, Fe_2O_3	3.5	3.6
Calcium oxide, CaO	1.1	1.0
Ferrous sulfate, $FeSO_4$	1.1	1.6
Calcium sulfate, $CaSO_4$	1.3	2.3
Aluminum sulfate, $Al_2(SO_4)_3$	0.7	1.3
Copper sulfate, $CuSO_4$	tr.	0.1
Absorbed water	1.4	2.1

While many common brick and tile can be boiled in sulfuric acid, without any signs of deterioration, they will often slowly disintegrate when exposed to gases from smelting-plant furnaces. In the case of three reverberatory furnace flues and two roaster dust chambers and flues where ordinary red building tile were used instead of brick, the reverberatory flues carrying the gases between the waste-heat boilers and the smoke stack, one flue had to be reconstructed within two years, one has been in operation five years, and the third seven years, without any apparent deterioration in the structure of the tile. The tile in both roaster dust chambers and flues have given trouble and a number of sections have been replaced or repaired. The rapid deterioration of the first flue was probably due to the cooler gases because fewer furnaces discharge into it than into the others.

When tile are exposed to the deleterious action of the gases, their thin walls gradually disintegrate and finally fail. Brick are more satisfactory for the walls of flues and dust chambers than tile. Brick exposed to low-temperature gases disintegrate in the same way, but the rate of disintegration is gradually reduced so that many years pass before the brick are injured sufficiently to cause them to fail.

TILE-LINED STACK FOR BLAST AND REVERBERATORY FURNACES

At the same plant, a steel chimney, 25 ft. 9½ in. (7.8 m.) in diameter by 305 ft. (92.9 m.) high, Fig. 2, lined with hollow building tile, has been in use since June, 1913. The lining is still in place and no deterioration of any part of the structure is apparent. This stack is used for discharging the gases from blast furnaces and reverberatory furnaces, which are hotter than the gases in the roaster stack.

BRICK-LINED BLAST-FURNACE STACK

At Cananea, a steel chimney 19 ft. 9 in. (6 m.) in diameter by 170 ft (51.8 m.) high was put into service in 1903 in connection with the blast

furnaces; it is lined with common brick. The lining of the lower 85 ft. (25.9 m.) is 6 in. (15 cm.) thick, being made of blocks 2½ by 6 by 12 in.; the lining of the upper 85 ft. is 4½ in. thick, being made of blocks 2½ by 4½ by 12 in. All blocks are made radial to suit the circle in which they

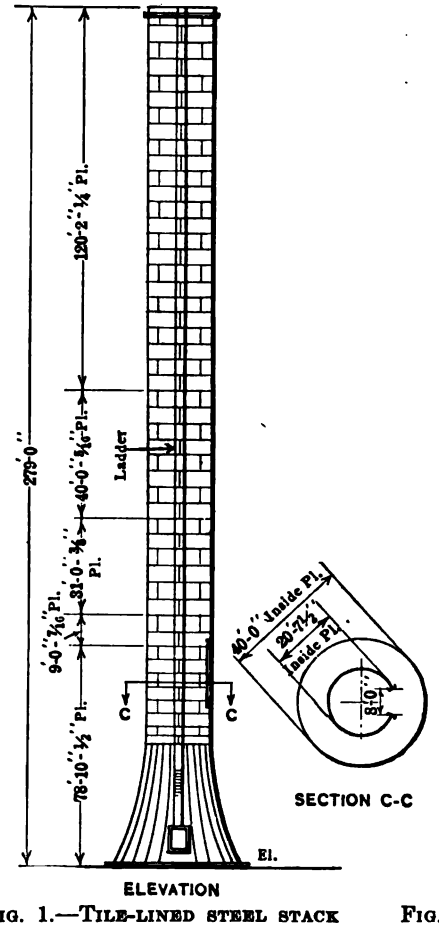

FIG. 1.—TILE-LINED STEEL STACK USED FOR ROASTER GASES.

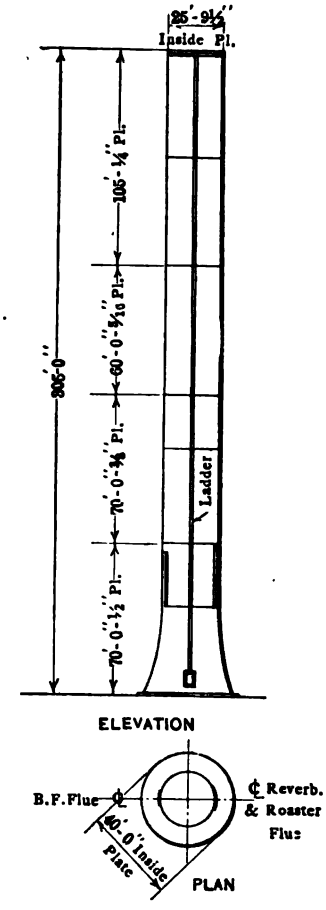

FIG. 2.—TILE-LINED STEEL STACK FOR BLAST AND REVERBERATORY FURNACES.

are laid. This chimney has been cold a number of times for periods of from several days' to a year's duration, but there is no apparent deterioration.

BRICK-LINED STACK FOR VARIOUS FURNACES

At the United Verde Copper Co.'s smelting plant at Clarkdale, Ariz., a steel chimney 30 ft. 9½ in. (9.3 m.) in diameter and 400 ft. (121.9 m.)

high, Fig. 3, was put into service in June, 1915. The gases from the blast, roaster, and reverberatory furnaces and the converters pass through it. The 4½-in. brick lining is supported on angle iron rings 15 ft. apart. Recently ½-in. test holes, drilled in the steel shell at intervals all the way to the top, showed no signs of corrosion.

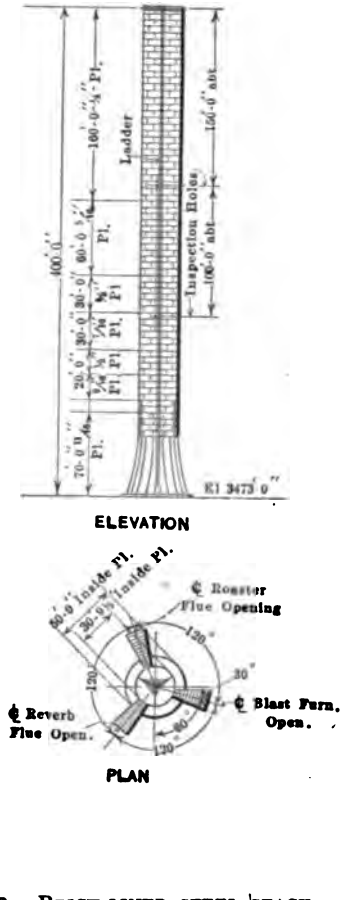

FIG. 3.—BRICK-LINED STEEL STACK FOR VARIOUS FURNACES.

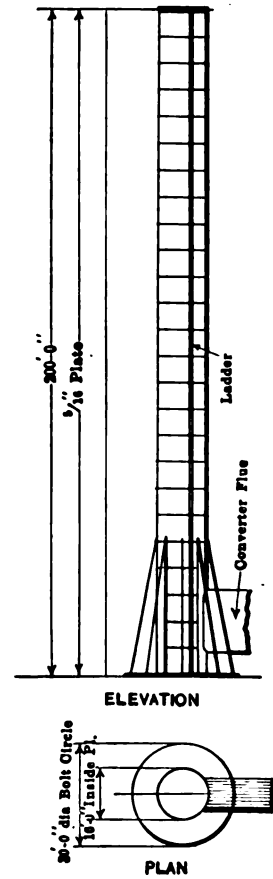

FIG. 4.—UNLINED STEEL STACK USED FOR CONVERTER GASES, BUILT AS BLAST-FURNACE CHIMNEY.

UNLINED STACKS FOR CONVERTER GASES

At the Calumet & Arizona plant at Douglas, there is a steel chimney, 15 ft. (4.5 m.) diameter by 200 ft. (60.9 m.) high, Fig. 4. It has been unlined since it was erected at the original plant of the company, in 1906, as a chimney for the blast furnaces. In the latter part of 1913, this plant was shut down, so the chimney was dismantled and re-erected at the new

plant where it has served as the converter department chimney. It is still in apparently as good condition as when new.

At the International Smelting Co.'s plant, at Miami, a steel stack, 15 ft. diameter by 200 ft. high, Fig. 5, is used for discharging the gases from the converter department. It is unlined and has been in use since May, 1915, except during a six weeks' strike in the rainy season. At present it shows no signs of deterioration.

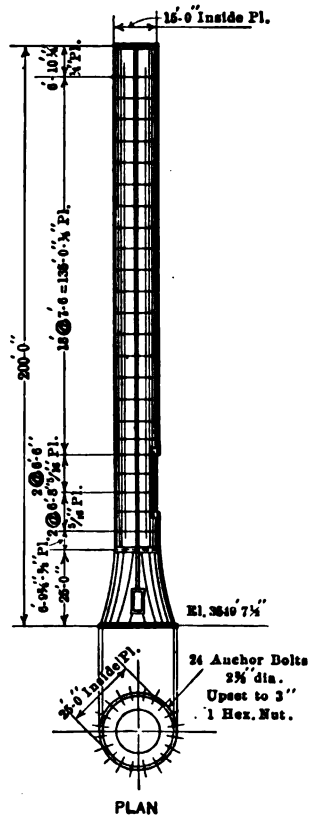

FIG. 5.—UNLINED STEEL STACK USED FOR CONVERTER GASES.

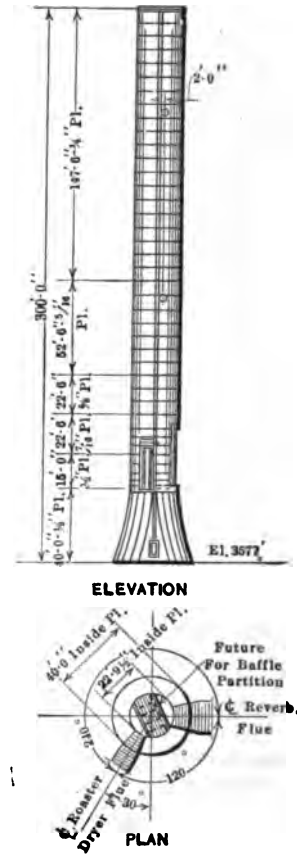

FIG. 6.—PARTLY LINED STEEL STACK FOR REVERBERATORY FURNACE.

UNLINED STACKS FOR BLAST FURNACES AND CONVERTERS

At Morenci, Ariz., the Detroit Copper Co. put into operation, in September, 1899, an unlined steel stack, 13 ft. (3.9 m.) diameter by 165 ft. (50 m.) high, to discharge the gases from copper blast furnaces and con-

verters. It has been cold during several periods on account of strikes. At the present time, the stack is in good condition, with the exception of the upper 12 ft., where it has commenced to deteriorate quite badly since the plant was shut down eight months ago.

At the Copper Queen smelting works in Douglas, an unlined steel chimney, 25 ft. (7.6 m.) in diameter by 260 ft. (79 m.) high, was put into service in June, 1904, to discharge the gases from the blast furnaces and converters. A recent investigation showed that the interior was coated with flue dust, about 2½ in. (6.35 cm.) thick, but that the steel is of its original thickness. The chimney has not been cold since 1906. The minimum temperature of the gases in this chimney is 325° F.

At the Old Dominion smelting plant in Globe, an unlined steel stack 14 ft. (4 m.) in diameter by 200 ft. (60.9 m.) high, has been in use since August, 1904, to carry the gases from the blast furnaces and converters. The plant has been shut down several times, once for six weeks during the rainy season, but the stack shows no deterioration.

Unlined Stacks for Reverberatory Furnaces

At the International Smelting Co.'s plant at Miami, Ariz., a steel chimney 22 ft. (6.7 m.) in diameter by 300 ft. (91 mi.) high, Fig. 6, discharges the gases from the reverberatory furnaces. When the chimney was built, it was thought that a lining would not be required but as the reverberatory furnaces have waste heat boilers installed between them and the flue leading to the chimney and as there was a possibility that the boilers might be bypassed at some time and the hot gases from the reverberatory furnaces allowed to go directly to the stack without much cooling, it was decided to line the lower 100 ft. In the bell, common red brick was used; above the bell common red building tile 4 in. thick was used. The chimney was put into use in May, 1915. In 1917 the plant was shut down, on account of a strike, for six weeks during the rainy season. About a year later, it was noticed that certain sheets had become distorted and an investigation showed that the steel sheets above the lining were seriously weakened from corrosion. A temporary repair was made by reinforcing the chimney for 75 ft. with an outer steel shell. As corrosion is continuing, a new radial brick-tile chimney is being built to replace the steel chimney.

A steel chimney at the reverberatory furnace plant of the Cananea Consolidated Copper Co. 12 ft. (3.6 m.) in diameter by 171 ft. (52 m.) high, had a 9½-in. (24-cm.) firebrick lining in the lower half and a 4½-in. (12-cm.) firebrick lining in the upper half. This chimney was put into service in 1902, and after a year's service as a blast-furnace smokestack, it was unused until 1908, when it was put into service as a reverberatory furnace stack. In 1910, the reverberatory furnaces needed more draft so

the brick lining of the chimney was removed, as it was thought that reverberatory furnace gases would not injure the steel. In 1917, it was necessary to renew the upper 75 ft. of the stack, but the lower part of the stack had deteriorated but little. The stack was not relined.

Conclusion

Based only on the examples cited, the following conclusions may be drawn: Unlined steel chimneys have not given satisfactory service when used for roaster or reverberatory furnaces. Unlined steel chimneys have given satisfactory service for long periods when used for blast furnace and converter gases.

Building tile have proved unsatisfactory for chimney linings or for the construction of walls for flues and dust chambers where exposed to roaster furnace gases or cool reverberatory furnace gases.

These conclusions apply to the ordinary conditions in copper smelting plants, where waste-heat boilers are used in connection with reverberatory furnaces, and where no particular effort is made to maintain the gases at a high temperature in the flues, dust chambers, and stacks.

DISCUSSION

C. R. Kuzell, Clarkdale, Ariz. (written discussion).—In considering the possible deterioration of a steel stack, one may be guided by the presence in the ore of such impurities as zinc, which may be fumed off in certain furnace operations in sufficient quantities to neutralize the acid fumes.

The steel stack of the United Verde Copper Co. at Clarkdale, Ariz., mentioned by Mr. McGregor, handles the gases from all departments. As there is sufficient zinc fumed off in the blast furnace and converter operations to neutralize the gases, there has been no corrosion. However, the roaster gases are quite acid and, as no zinc is fumed off in the roasting operation, such gases if handled by a separate steel stack would likely corrode it. The rate of corrosion would be retarded in such a case by the installation of a Cottrell treater.

The conclusion that unlined steel chimneys have given satisfactory service for long periods when used for blast-furnace and converter gases is correct, but one can imagine cases in which this would not be so. For instance, corrosion could be expected in a stack handling untreated gases from the conversion of matte that did not contain fuming constituents, such as zinc and lead.

E. E. Thum, New York, N. Y.—The kind of smoke passing through and the outside atmospheric conditions are controlling factors in the life of a steel stack, although that fact is not brought out in the paper. In his conclusions, the author merely notes the fact that unlined steel

chimneys have not been satisfactory in roaster or reverberatory service. The paper shows that the deterioration is not so marked in one part of the stack as in another part; if the reason for this were determined, that information would be very valuable. Again, why should corrosion be severe during shutdowns?

Another curious fact is that roaster gas is not corrosive, whereas nearly all the published analyses show that roaster gases are usually high in sulfuric trioxid; the same is true of converter gases.

All who have handled converter gases from the hood to the main dust chamber in a steel balloon flue, or a flue with steel hopperbottom, know that there is always a great deal of corrosion around the hopper openings and other points where there is a little leak passing air or gas. Why converter gases should be so extremely corrosive close to the converter and yet not corrosive when they get into the stack is something which might well be elucidated. Corrodability of blast-furnace gas is unquestionably also greatly dependent on the content in basic fume, as Mr. Kuzell points out.

On the whole, the question of the life of steel flues and stacks depends primarily on the analysis of the gas to be handled, and only incidentally on the department from which it originates, or the geographical location of the smelter.

FOREST RUTHERFORD, New York, N. Y.—The main stack of the Copper Queen Smelter at Douglas, Ariz., is steel, unlined, and although in use since April, 1904, is apparently still in good condition. It was originally 25 ft. in diameter and 200 ft. in height, but afterwards 60 ft. were added to the height with a shutdown of the plant of approximately 6 hr. only. It takes the gases from the blast furnaces and converters, which are not extremely corrosive, but the long life of the stack is due to the fact that it has been in continuous operation and at a temperature above that at which sulfuric acid condenses.

The stack for the reverberatory furnaces and roasters is built of hollow radial tile and lined throughout with acid-resisting tile laid in acid-proof cement. At the time this stack was built, a dust chamber was put up, the walls and roof of which were of ordinary hollow building tile set in lime-cement mortar. It was soon found that these tiles were crushing and in fact that the chamber would have to be rebuilt. On investigation, it was found that the sulfuric acid in the roaster gases was combining with the lime in the mortar and with what little lime there was in the tiles, causing the joints to swell and thereby crush the tile. Practically no softening of the tile due to corrosion was evident.

I understand the Calumet and Arizona smelter roaster stack was lined with tile and lime-cement mortar and that some of the tile contained quite an amount of free lime, no doubt the experience was the same as

with the Queen dust chamber. The tile crushed and exposed the steel to the effects of the corrosive gases.

It would seem to be dangerous to use a steel stack for roaster gases, unless perfectly lined with acid-resisting materials, whereas for gases from blast furnaces, converters, and reverberatory furnaces, if the stack is kept hot, it does not matter much whether a steel stack is lined or not.

HIRAM W. HIXON, New York, N. Y.—This question of the corroding of the steel stack is dependent on the relative humidity of the atmosphere and the temperature of the gases in the stack. If the gases are always so hot that there is no condensation, there is no corrosion.

The reason converter gases attack one part of the stack and not another is that eddies are set up by the gases issuing from the mouth of the converter and the air taken in at the hood. There will be eddies and condensation at several points in the stack until the gases mingle, so that the temperature of the gases as a whole is above the condensation point of the moisture.

In Mexico, there was no corrosion in the bottom portion of an unlined steel stack and in the iron flue leading to it, where the temperature was sufficiently high, but there was corrosion near the top, particularly at the reinforcing band at the top, which fell off because the rivets were corroded. As the band was on the outside of the stack, it was in a lower temperature, besides there is a large rain-fall and the relative humidity was high. In other words, the condensation point was near the top of the stack, while in the flue the temperature was much higher and in the bottom of the stack.

It has been my experience that in very cold weather, in Canada, for instance, there would be condensation near the top of the stack, and consequently corrosion, especially when there was fog or rain. In Arizona, where the climate is dry, the stack would not be attacked. So that the life of the stack depends on the relative humidity of the gases in the stack and the air outside; if there is condensation the stack is attacked, if there is no condensation, the stack is not attacked.

E. H. ROBIE, New York, N. Y.—The composition of the iron and steel probably has something to do with the corrosion in stacks. At the International nickel smelter at Copper Cliff, four Wedge furnaces have been installed about 7 years; the steel balloon dust chamber connected with a stack about 150 ft. high, was corroded through in many places in 5 years. Almost every section is now badly corroded, but the steel stack, when I saw it two years ago, was still in good condition. The temperature of the gases in the balloon flue would be somewhat higher than the temperature of the gases in the stack, and the gases would be of exactly the same composition, because no other gases were entering that stack. Apparently, therefore, the material of the dust chamber was less resistant.

A. G. McGREGOR (author's reply to discussion).—It is quite possible that Mr. Kuzell is right in his contention that the presence of zinc and lead fumes in the furnace and converter gases neutralizes their corroding effects on steel chimneys and flues. At the Calumet & Arizona plant the relative lead and zinc content of the roaster gases is considerably less than it is in the converter and blast-furnace gases.

In answer to Mr. Thum, I believe corrosion in flues, etc., during shutdowns will not amount to much if they are protected from the weather. Dry flue dust is not corrosive, but when moistened with water, it is an active corrodent.

In a flue unprotected from the weather, there is no heat present during a shutdown to prevent the rain from readily moistening flue dust lodged on the outside of the flue or in the joints. Rain also leaks through the top of a flue to the dust inside. In this way steel flues are damaged inside and outside during shutdowns.

In the case mentioned by Mr. Robie, it is quite likely that the flue is exposed to the weather, and is rained upon occasionally. Ordinarily, during dry weather, in flues of this kind, the steel sheets comprising the walls and tops of the flues are maintained at a sufficiently high temperature by the gases inside, so that the gases in contact with the sheets are not condensed and no harm to the sheets results. But when it rains, the sheets exposed are cooled and the gases adjacent to them apparently condense and cause corrosion. The corrosion occurs almost altogether on the inside, and the sheets in the top, which are more effectively cooled by rain, are generally much more rapidly corroded than the sheets forming the sides of such flues.

It is the writer's belief that if the temperature of smelting-furnace gases is maintained above the condensing temperature of sulfuric acid, the vertical walls of flues and stacks conducting them will last indefinitely, and it is probable that if the lead and zinc content of the gases is relatively high, a lower temperature may be permitted without injury to the steel.

John Stewart MacArthur

A BIOGRAPHICAL SKETCH BY ALFRED JAMES

JOHN STEWART MACARTHUR, born in 1856, was the son of Robert MacArthur of Glasgow, and came of Scots stock distinguished for character and religious conviction. His election as elder of the Free Kirk gave him greater pride than the receipt of the gold medal of the Institution of Mining and Metallurgy. The former honor was for character—it marked him as a son worthy to follow in his father's footsteps; the latter was awarded for his life work of eminent service to the gold industry. Cheery optimism, resolution, tenacity of purpose, and industry ever characterized his actions.

Apprenticed to the Tharsis Sulphur & Copper Co., his work on the chemical staff brought him to the notice of the Cassel Gold Extracting Co., at that time struggling with an unworkable electrolytic process. He was engaged by that company, in 1886, as technical manager and before long brought out the perchloride process, which was speedily followed (in 1887) by the epoch-making cyanide process. This process revolutionized gold mining and directly led the way to the elevation of the mining engineer to the most broadly trained product of the engineering profession.

A noteworthy feature of the cyanide process was its completeness when introduced. Over thirty years have elapsed and the use of the process has been worldwide, but no suggested improvement has stood the test of time. The extension of the process to the beneficiation of silver ores—containing far more metal per ton and thus requiring the employment of stronger solutions—has brought us the Merrill and Crowe improvements in precipitation and the Nipissing desulfurization process for certain silver-bearing minerals. Roasting apparatus, fine crushing, filtration, and settling equipment have all aided the extension of the process in and from its original field. As Hennen Jennings put it, the cyanide process today is essentially that of 1890.

This self-containedness of the cyanide process arose from no mere chance; it was directly due to MacArthur. It was he who personally investigated every known method of precipitation and then every form of zinc from sheet, punchings, filings, millings, rods and shaving down to fume; it was he who investigated the effect of protective alkalies, of so-called accelerators, and of the addition of lead salts; he was determined to leave nothing to chance.

South Africa honored MacArthur by making him an honorary member of the world-famous CM_2S, the well-known textbook on Rand metallurgy was dedicated to him; and Doctor Green's Presidential Address to the S. A. Association for the Advancement of Science contains the following tribute to his work: "Thus the development of the whole mining industry of the Witwatersrand . . . was conditioned by a laboratory observation."

But MacArthur was too keen a scientist to rest content with the successful development of the cyanide process. He traveled much, and interested himself in the mining and metallurgy of base metals. His friendship with Sir William Crookes and his flair for investigation caused him in 1910 to devote himself to the investigation of radium. At Runcorn, he set up experimental works which justified all his hopes. The difficulties of evolving a process, designing equipment, training staff for an absolutely new industry, all disappeared before the tenacity of his resolution. These works were transferred to Balloch, in 1915, and practically the whole of the output was used for war purposes, Sir William Ramsay, at the nomination of the Government, coöperating with him for the purpose.

His death at his home at Pollokshields on March 16, 1920, was the result of complications following a chill. His only son, Mr. J. S. MacArthur, now a classical exhibitioner at Balliol College, Oxford, will realize in years to come that his father has left behind a heritage of friendships which will not fail him but will welcome his presence and his every achievement.

INDEX

[NOTE.—In this Index the names of authors of papers are printed in small capitals, and the titles of papers in italics. Casual notices, giving but little information, are usually indicated by bracketed page numbers.]

Acidity of solution, electrolytic zinc: effect on current efficiency, 743, 744.
effect on power, 751.
Addition agents, electrolytic zinc, 731, 761.
Admiralty bronze, 378.
Aging, duralumin, 43.
ALDERSON, G. E.: *Discussion on Reclamation of Metal from Brass-foundry Refuse*, 660, 661.
ALDERSON, G. E. and WOLF, F. L.: *Reclamation of Metal from Brass-foundry Refuse*, 650.
ALEXANDER, JEROME: *Colloidal State in Metals and Alloys*, 524; *Discussion*, 551.
ALLIS, F. G.: *Discussion on Charpy Impact Test as Applied to Aluminum Alloys*, 482.
Allocolloids, 525.
Allotropism, lead, 447.
Alloys, see under names and constituent metals.
Alloys, colloidal state, see *Colloidal state, metals.*
Alpha brass, grain growth, 159.
Aluminum: bending curves, slow, 475.
commercial: constitution, 4.
cooling curves, 7.
photomicrographs, 5.
silicon content, effect, 7.
compounds with metals, 3.
copper content, effect, 283.
effect in rolled zinc, 319.
melting: borax cover, 670.
impurities introduced, 664, 665.
Aluminum-alloy castings: copper content, effect, 277.
heat treatment, 270.
iron content, effect, 277, 281.
magnesium content, effect, 277, 278, 281.
mechanical properties, 272.
microstructure, heat-treatment effect, 284.
oxidation, 271.
photomicrographs, 285.
porosity, 271.
quenching, 271.
tensile tests, 272.
Aluminum alloys: bending test, slow, 469, 472, 476, 479.
binary system characteristics, 3.
Charpy impact test: 466.
comparisons with other tests, 474, 477.
duralumin, heat treatment, 43.
etching, 25.
hardening, 270.
light, composition, 31, 32.
microscopic identification of constituents, 21, 25.
rolled: corrosion, relative, 38, 39.
corrosion tests, 36.
hardening effect of alloying elements, 35.
preparation, 30.
tensile strength increase by heat treatment, 35.
Aluminum cathode sheets, electrolytic zinc, 701, 727.

Aluminum Co. of America: duralumin investigations, 42.
investigations of rolled aluminum alloys, 30.
Aluminum-copper alloys: equilibrium, 9, 14, 62.
equilibrium diagram, 62.
hardness, 474.
mechanical properties, 474.
photomicrographs, 10, 12.
Aluminum-iron-copper alloys, liquidus surfaces, 74.
Aluminum-iron-silicon system, liquidus surfaces, 8.
Aluminum-magnesium alloys: equilibrium, 15, 18.
photomicrographs, 16.
Aluminum-magnesium-copper alloys: equilibrium diagram, 62.
heat treatment, 43.
properties, 33, 44.
Aluminum-magnesium-manganese alloys, mechanical properties, 32.
Aluminum-magnesium-nickel alloys, mechanical properties, 34.
Aluminum Manufactures, Inc., Charpy impact tests, 466.
Aluminum sulfate, copper leaching, 573.
Aluminum wire: elongation, 807, 810, 811, 812.
fracture, photographs, 786.
mechanical properties, at various temperatures, 799.
reduction of area, 808, 811.
tensile strength, 806, 809, 810, 812.
Aluminum-zinc alloys, 320.
Amalgamation, silver-tin ores, Bolivian, 677.
Amalgams .dental, see *Dental amalgams*.
American Foundrymen's Association, joint meetings with Institute of Metals Division, [vii].
Ammonia, deoxidation of copper, 672.
Amorphous theory, metals: application to lead, 459.
colloidal state of particles, 524, 529.
crystallization, 529, 530.
structure, 325.
zinc properties, 328.
Ampere efficiency, electrolytic zinc, 743, 744.
Anaconda Copper Mining Co.: electrolytic zinc, 699.
reverberatory furnace for converter slag, 585.
Analysis: antimony ore, 566.
cement copper briquettes, 82.
chimney lining, Calumet & Arizona smelter, 831.
coke, byproduct, 647.
coke-oven gas, 648.
constantan, 241, 258.
converter slag, smelting charge and products, 593, 594.
copper, electrolytic, 435.
copper ores, Consolidated Coppermines Co., 818, 819.
dental amalgams, 489.
duralumin, 43.
dust, Cottrell treaters, cement plant, 777, 778.
electrolyte, copper leaching, 578.
flue-dust, Tooele smelter, 770.
foundry refuse, reclamation products, 654.
manganin, 262.
nichrome, 559.
nickel, commercial forms, 391, 392, 394.
nickel silver, 510.
nickel wire, 132.
producer gas from coke, 649.
thermal, see *Thermal analysis*.
tin filling, fusible boiler-plugs, 230, 231, 232.
wash water, copper leaching, 576.
zinc ores, electrolytic tests, 87.
Annealing: brass: grain growth, 159.
macrographs, 160.
photomicrographs, 168.
constantan, 242.

Annealing: copper, 436.
gun metal, effect, 294.
manganin, 262.
nickel, 414, 417.
rolled zinc, effect, 314, 341, 347, 352, 356.
zinc strip, effect, 341, 347, 352, 356.
Anodes, electrolytic zinc process, 701, 728.
Antimonial lead, International Lead Refining Co., 566.
Antimony ore: analysis, 566.
smelting, International Lead Refining Co., 566.
Antimony-tin alloys, freezing-point curve, 233, 237.
ANTISELL, FRANK L.: *Relationship of Physical and Chemical Properties of Copper*, 432.
Discussion on Intercrystalline Brittleness of Lead and Copper, 462.
Assay muffle fume, 604.
Assaying: condensation of muffle fumes, 604.
dusting loss, 603.
feathering, 612.
recoveries, 613.
spitting of silver, 610.
volatilization, 601, 602, 603, 610, 614.
Atomic weight, nickel, 393.
Austenite, 537.
AUSTIN, W. L.: *Discussion on Chemical and Electrochemical Problems Involved in New Cornelia Copper Co.'s Leaching Process*, 583.

Bag house, Great Falls electrolytic zinc plant, residue treatment, 735, 737, 738.
BASH, F. E.: *Manufacture and Electrical Properties of Constantan*, 239.
Manufacture and Electrical Properties of Manganin, 261; *Discussion*, 268, 269.
BASSETT, W. H.: *Discussions:* on *Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals*, 815.
on Five Foundry Tests of Zinc Bronzes, 385.
on Manufacture and Electrical Properties of Manganin, 269.
on Physical Properties of Nickel, 418.
on Relationship of Physical and Chemical Properties of Copper, 436.
Bending properties, rolled zinc, 354.
Bending test, slow: aluminum, 475.
aluminum alloys, 469, 472, 476, 479.
BENEDICKS, CARL: *Discussion on Colloidal State in Metals and Alloys*, 549.
BERRY, W. V.: *Discussion on Investigation of Brass Foundry Fluxes*, 675.
Biographical notice, MacArthur, John Stewart, 840.
Blast furnace, antimonial lead smelting, International Lead Refining Co., 567.
Blast-furnace gases, steel chimneys, 831, 834.
Blast-furnace slag: copper content, form, 597.
magnetite content, 599.
BLIEK, P. F.: *Discussion on Roasting and Chloridizing of Bolivian Silver-tin Ores*, 694.
Boiler-plugs, fusible: casing material, 228.
manufacture, 227, 235.
photomicrographs, casing and filling, 229.
precautions in manufacture, 235.
specifications, 227, 228.
testing: Bureau of Standards, 227.
rejection causes, 227.
tin filling: freezing points, 232, 236.
purity, 231, 237.
solution of zinc and copper from casing, 232.
temperature effects in manufacture, 230, 231.
Boiling points, chlorides, 83.
Bolivia, silver-tin ores, roasting and chloridizing, 676.
Bonnet pulverizer, pulverized coal, 623.
Borax cover in melting metals, 670, 675.
Brass: annealing, crystalline growth, 159.
ductility, static and dynamic, 366.
grain growth after annealing, 159.
large grain formation, 186.
macrographs, structure after annealing, 160.
molten: gases contained, 666.
hydrogen evolution, 667.

Brass: phases, 535.
photomicrographs, structure after annealing, 168.
Brass foundry: fluxes, 662.
reclamation of metal from refuse, 650.
BREYER, F. G.: *Discussions: on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 755, 756.
on Some Applications of Rolled Zinc Strip and Drawn Zinc Rod, 377.
BRIDGMAN, P. W.: *Discussion on Colloidal State in Metals and Alloys*, 546.
Briquets: cement copper, see *Cement copper briquets.*
zinc ore, electric distillation, 188, 191, 192, 196, 199.
Brittleness: intercrystalline: copper, 439.
lead, 443.
lead, experimental production, 447.
Bronze: Admiralty, 378.
annealing, effect, 294.
composition diagram, 424.
Government, 378.
heat treatment, tests, 293.
lead-zinc, see *Lead-zinc bronze.*
nickel content, effect, 430.
quenching, effect, 293.
zinc, see *Zinc bronze.*
BROWNE, DAVID H. and THOMPSON, JOHN F.: *Physical Properties of Nickel*, 387.
BULLOCK, STANLEY C.: *Discussion on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 753.
Bully Hill ore, electrolytic zinc research, 85, 87.
Bureau of Standards: boiler-plug testing, 227.
duralumin investigations, 42.
BURGESS, G. K.: *Discussions: on Heat Treatment of Aluminum-alloy Castings*, 289.
on Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, Nickel and Manganese, 40.
Butte zinc ore, treatment possibilities, 699.
Byproduct coke oven: coke: analysis, 647.
physical properties, 647.
quality, 640.
control, 641.
gas: analysis, 648.
use as metallurgical fuel, 644.
pitch: properties, 648.
viscosity, 641.
products, quantities, 640.
tar: properties, 648.
use as metallurgical fuel, 643.
viscosity, 641.

Cadmium: effect in zinc electrolyte, 730.
precipitation in electrolytic zinc process, 717.
CAESAR, G. V.: *Discussion on Relationship of Physical and Chemical Properties of Copper*, 436.
CALLOW, J. M.: *Discussion on Treatment Tests on Ores of Consolidated Coppermines Co.*, 828.
Calumet & Arizona Mining Co., steel chimneys, 830.
CAPLES, R. B. and ELTON, J. O.: *Discussion on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 758.
CAPLES, R. B., LAIST, FREDERICK, FRICK, F. F. and ELTON, J. O.: *Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 699.
Carbon, effect in nickel, 408.
CARTER, F. E.: *Discussion on Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals*, 815.
Casting: copper, 434, 437.
fluxing, see *Fluxing, foundry.*
zinc, electrolytic, 732, 733.
Castings, aluminum-alloy, see *Aluminum-alloy castings.*
Cathode: copper, see *Copper cathode.*
lead, see *Lead cathode.*
Cathode sheets, electrolytic zinc, 701, 727.

Cement copper briquets: analysis, 82.
chlorine content, 82.
oxidation in drying, 81.
sampling, 81.
water content, 81.
Central Mining Co., electrolytic zinc, 756.
Charpy impact test, aluminum alloys: apparatus, 466.
material, 469.
results, 471.
test specimens, 468.
Charpy Impact Test as Applied to Aluminum Alloys (Dix), 466; *Discussion:* (Dix), 481, 482; (Merica), 481; (Allis), 482.
Chemical action of fluxes, 668.
Chemical and Electrochemical Problems Involved in New Cornelia Copper Co.'s Leaching Process (Mackay), 568; *Discussion:* (Austin), 583.
Chilling, metals, effect on physical properties, 526.
Chimneys: blast-furnace gases, 831, 834.
brick lining, 831, 832.
converter gases, 833, 834.
lining: analysis, Calumet & Arizona plant, 831.
deterioration, 831.
reverberatory gases, 831, 835.
steel: Copper Queen smelter, 837.
deterioration, 830, 836, 837, 838.
International Smelting Co., 834.
roaster gases, Calumet & Arizona Mining Co., 830.
unlined, 833.
tile lining, 831.
Chloride fluxes, chemical action, 668.
Chlorides: in cement copper briquets, 82.
melting and boiling points, 83.
volatility, 83.
Chloridizing: dust losses, 681.
hand-rabbled furnace, 678.
McDougall furnace, 680.
mechanical furnace, Machacamarca, 680.
Merton furnace, 684.
silver-tin ores, Bolivian, see *Silver-tin ores.*
straight-line furnace, 683.
volatilization losses, 681.
Chlorine, effect in electrolytic zinc solution, 730.
Chrome-nickel steel, see *Nickel-chromium steel.*
Chromium alloys: resistivity, 561.
temperature coefficients, 564.
Chromium-nickel alloys, see *Nickel-chromium alloys.*
Chronograph, use in thermal analysis, 26, 27.
Clamer, G. H.: *Discussions: on Intercrystalline Brittleness of Lead and Copper*, 460.
on Laboratory Testing of Sands, Cores, and Core Binders, 638.
on a New Process for Making Fifteen Per Cent. Phosphor-copper, 487.
on Reclamation of Metal from Brass-foundry Refuse, 660.
Classification, fluxes, 662.
Coal, pulverized, see *Pulverized coal.*
Coal-pulverizing Plant at Nevada Consolidated Copper Smelter (Pomeroy), 618; *Discussion:* (Tillson), 628; (Pomeroy), 628.
Coal tar, see *Coke-oven tar.*
Cobalt, effect in electrolytic zinc process, 700, 731.
Cohesion-temperature curves, amorphous and crystalline phases, 326.
Coke: byproduct, see *Byproduct coke.*
use in gas producers, 645.
Coke and Byproducts as Fuels for Metals Melting (Sperr), 640.
Coke oven, byproduct, see *Byproduct coke oven.*
Coke-oven gas: analysis, 648.
use as metallurgical fuel, 644.
Coke-oven tar and pitch: properties, 648.
use as metallurgical fuel, 643.
viscosity, 641.

Cold-bend values, zinc, rolled, 354.
Colloidal state: allocolloids, 525.
definition, 524.
dimensions, 524.
energy accumulation from surface tension, 547.
isocolloids, 525.
metals: amorphous phase, 524, 529.
brass, 534.
iron and steel, 535.
liquid state, 544.
surface tension effect, 547.
tin-lead alloys, 532.
phases, 524.
size of particles, 524.
solubility increase, 548.
vapor tension increase, 548.
Colloidal State in Metals and Alloys (ALEXANDER), 524; *Discussion:* (MERICA), 544; (THUM), 544; (JEFFRIES), 546; (BRIDGMAN), 546; (LE CHATELIER), 547; (BENEDICKS), 549; (ALEXANDER), 551.
Columbus meeting, 1920, viii.
Composition diagram, zinc bronze, 424.
Composition test, foundry sand, 631.
COMSTOCK, G. F.: *Discussion on Influence of Heat Treatment on Gun Metal*, 302.
COMSTOCK, G. F. and WILSON, A. B.: *Discussion on Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium*, 21.
Concentration: foundry refuse, reclamation of metal, 652, 659, 660, 661.
Steptoe Reduction Works, 817.
Conductivity: electrical, copper, 435.
thermal, nickel, 399.
Consolidated Coppermines Co.: flotation, 820.
flow sheets, 817, 822.
history, 816.
Minerals Separation machine tests, 825.
ore, classification and composition, 818.
ore testing, 816.
remodeled mill, results, 820.
Constantan: annealing, 242.
composition, 241, 258.
electrical properties, 239.
e.m.f. measurements, 254.
impurities, effects, 245.
manufacture, 239.
melting, 251.
photomicrographs, 248.
specifications, 239.
wire tests, 257.
Constituent forms of iron carbide dispersion, 539.
Constitution: aluminum, commercial, 4.
aluminum alloys with copper and magnesium, 3.
duralumin, 41.
Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium (MERICA, WALTENBERG and FREEMAN), 3; *Discussion:* (COMSTOCK and WILSON), 21; (MERICA), 25.
Control, copper leaching process, points involved, 569.
Converter gases, steel chimneys, 833, 834.
Converter slag: disposal methods, 598.
reverberatory smelting: analyses, 593.
equipment, Anaconda, 587.
experimental data, 586.
furnace, 587.
magnetite content, 596, 597, 598.
operation, 590.
results, 591.
Cooling curves: aluminum, commercial, 7.
dental amalgams, 499.
duralumin, 63.

Copper: annealing, 436.
brittleness, intercrystalline, 439.
casting, 434, 437.
cement, see *Cement copper.*
chemical and physical properties, relationship, 432.
conductivity, electrical, 435.
effect in aluminum alloys, 277, 281, 282.
effect in commercial aluminum, 283.
effect in electrolytic zinc solution, 729.
effect in rolled zinc, 321, 322.
electrolytic, analysis, 435.
embrittled, photomicrographs, 440, 464.
hydrogen content, effect, 461, 462.
leaching, see *Leaching process, copper.*
melting: deoxidation, 671, 672.
sodium chloride action, 80.
molten: gases contained, 666.
hydrogen evolved, 667.
oxygen content, influence, 433, 435.
phosphor-copper, 483.
phosphorization, 484.
physical properties, 432.
pitch, 432.
pouring method, 437.
precipitation in electrolytic zinc process, 718.
reaction with sodium chloride, 80.
rejecting, reasons, 434.
reverberatory slag, form, 597.
set, 432.
specifications, 432.
sulfur content, effect, 433.
unhealthy, 433.
Copper-aluminum alloys: equilibrium, 9, 14.
equilibrium diagram, 62.
hardening, 270.
photomicrographs, 10, 12.
Copper-aluminum-magnesium alloys, mechanical properties, 33.
Copper cathode: embrittlement in fused-salt electrolyte, 439.
fused-salt cell, photomicrographs, 441.
Copper-nickel alloys, thermo-electromotive force against iron, 243.
Copper ores, analysis, Consolidated Coppermines Co., 818, 819.
Copper Queen smelter, chimneys, 837.
Copper-tin alloys: equilibrium diagram, 421.
freezing-point curve, 233.
Copper-tin-zinc composition diagram, 424.
Core, foundry, ideal properties, 631.
Corrosion: aluminum alloys, relative, 38, 39.
lead sheathing, 443.
steel chimneys, 836, 838.
Corrosion tests, aluminum alloys, rolled, 36.
Corse, W. M.: *Discussions: on Five Foundry Tests of Zinc Bronzes*, 385, 386.
on Influence of Heat Treatment on Gun Metal, 302.
on Physical Properties of Certain Lead-zinc Bronzes, 430.
Costs: electrolytic zinc, 758.
reclamation of metal from foundry refuse, 655.
Cottrell process: cement plant: analysis of dust, 777, 778.
potash recovery, 777.
chloridizing-roasting dust collection, 681.
Cottrell treater: flue-type, Tooele: description, 764.
electrical equipment, 769.
operation, 769.
potash precipitation, 777.
precipitation characteristics of dust and fume, 772.
Riverside Portland Cement Co., 775.
sections, 766, 768, 774, 775, 776.
Covers in melting, fluid, 670.

COWAN, W. A.: *Discussion on Tin Fusible Boiler-plug Manufacture and Testing*, 236.
Crushing, silver-tin ores, Bolivian, 693.
Crystal growth: brass, after annealing, 159.
dental amalgams, 489.
factors affecting process, 528.
metals, mechanism, 528.
Crystallinity of molecules, 529.
Cupel furnace, fume data, 603.
Cupellation, see *Assaying*.
Cyanide process: introduction, 840.
silver-tin ores, Bolivian, 677.

DAVIDSON, PHILIP: *Discussion on Physical Tests on Sheet Nickel Silver*, 523.
DAVIDSON, PHILIP and PRICE, W. B.: *Physical Tests on Sheet Nickel Silver*, 510.
Discussion on Physical Properties of Nickel, 414.
Decoloring power, nickel, 408.
Decomposition pressures, sulfates, 107, 108.
DEMMLER, P. E.: *New Process for Making Fifteen Per Cent. Phosphor-copper*, 483; *Discussion*, 486, 487.
Density, duralumin, 55.
Dental amalgams: composition, 489
cooling curves, 499.
crystal growth during transition, 489.
packing pressure, effect, 502, 505.
Roberts-Austen method of analysis, modified, 497.
thermal analysis, 488.
thermal expansion, 492.
transition phenomena, 488, 489
uniformity, 501, 508.
zinc as a constituent, 488, 504.
Deoxidation, by alloying metals, 672.
Deoxidizers: ammonia, 672.
copper melting, 671.
foundry fluxing, 670.
Deterioration of Nickel Spark-plug Terminals in Service (RAWDON and KRYNITZKY), 129; *Discussion:* (SILSBEE), 156; (MERICA), 157.
DEWEY, FREDERIC P.: *Volatilization in Assaying*, 601; *Discussion*, 617.
Dilatometric method, thermal analysis, 488.
Distillation, zinc, electric, see *Zinc, distillation, electric.*
DIX, E. H., JR.: *Charpy Impact Test as Applied to Aluminum Alloys*, 466; *Discussion*, 481, 482.
DRIVER, F. L.: *Discussion on Manufacture and Electrical Properties of Manganin*, 269.
Dryers, Ruggles-Coles, 621.
Ductility: dynamic, zinc, 359.
rolled zinc: at various temperatures, 312, 334.
effect of annealing, 356.
static and dynamic, zinc and brass, 366.
zinc, static and dynamic tests, 363.
Dust and fume, precipitation characteristics, 772.
Dust losses, chloridizing, silver-tin ores, 681.
Duralumin: aging, 43.
aging in quenching bath, 51.
aging temperature effect, 49, 50, 56, 57.
aging time effect, 51, 52, 56, 57.
composition, 43.
cooling curves, 63.
copper content, effect, 46.
density, 55.
dilatation, 55.
eutectic structure, 72.
expansion, 58, 59.
hardening, 41, 270.
analogy with steel, 71.
during aging, mechanism, 61.
hardness, 44.
heat treatment, 43.

Duralumin: magnesium content, effect, 46, 72.
microstructure, 65.
photomicrographs, 67.
preheating effect, 53, 54.
quenching temperature effect, 46, 47, 51, 52, 53.
resistivity, electrical, 59, 60.
structure, 65.
tensile properties, 44.

Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals (SYKES), 780; *Discussion:* (JEFFRIES), 814, 815; (BASSETT), 815; (CARTER), 815; (SYKES), 815.
Electric furnace, zinc roasting, experimental, 85.
Electric-resistance Furnace of Large Capacity for Zinc Ores (FULTON), 188; *Discussion:* (RICHARDS), 224, 225, 226; (TUCKER), 224; (FULTON), 224, 225, 226.
Electric zinc distillation, see *Zinc, distillation, electric.*
Electrical properties: constantan, 239.
manganin, 261.
Electrochemical problems, copper leaching, 568.
Electrode cooler, Jackson, 207.
Electrolytic copper, analysis, 435.
properties, 432.
Electrolytic deposition, copper, leaching process, 578.
Electrolytic nickel, 391.
Electrolytic zinc: acidity of solution: effect on ampere efficiency, 743, 744.
effect on power, 751.
addition agents, 731.
aluminum cathode sheets, 701, 727.
ampere efficiency, effect of acid in solution, 743, 744.
Anaconda, experimental plant, 702.
anodes, 701, 728.
Bully Hill ores, 85, 87.
cadmium precipitation, 717.
casting, 732, 733.
cathodes: starting, 701, 727.
time of deposition, 701.
Central Mining Co., 756.
copper precipitation, 718.
costs, high- vs. low-density plant, 759.
current density, high vs. low, 757, 758.
electrical units, Great Falls plant, 723.
electrolyzing: addition agents, 731.
anodes, 701, 728.
cathodes, 727.
cathodes, aluminum, deterioration, 727.
glue, 728, 756, 757, 761.
Great Falls plant, 721.
impurities, 729.
insulation, 729.
manganese dioxide deposition, 729.
operation, 724.
solids in suspension, 731.
tank attendance, 726.
temperature, 731.
English practice, 753.
experimental plant, Anaconda, 702.
extraction, 755.
flow sheet, Anaconda Copper Mining Co., 715, 720.
foreign practice, 753.
glue in electrolyte, 728, 756, 757, 761.
Great Falls plant: bag house, 735, 737, 738.
electrical units, 723.
electrolyzing division, 721.
flow sheet, 715, 720.
leaching division, 711.
melting division, 732.

Electrolytic zinc: Great Falls: plant: operating data, 739.
plan, 703.
power distribution, 752.
purification system, 719.
residue treatment, 735.
roasting division, 703.
slime from purification of solution, treatment, 721.
view of, 701, 702.
zinc-dust plant, 734.
impurities, behavior in roasting, 110.
impurities in electrolyte: cobalt, 700, 731, 755.
effect, 699, 700, 729, 754.
manganese, 701, 729, 730.
precipitation, 717, 718.
leaching: acid leach, 715, 716, 717.
copper and cadmium purification, 717.
diagrams of chemistry of process, 717.
neutral leach, 711, 714, 717.
operation, 711.
plant diagrams, Great Falls, 711, 712.
repulping, 715, 716, 717.
solution of impurities, 716, 717.
zinc-dust precipitation, 717.
manganese function, 701, 730.
Martinez plant, 755.
melting of cathodes: casting, 733.
charging, 733.
equipment, 732, 734.
reverberatory furnaces, 732.
sampling, 733.
mist in cell rooms, 756, 761.
operating data, Great Falls plant, 739.
ores tested, analysis, 87.
power cost, acidity effect, 751.
power efficiency, 748.
power distribution, Great Falls plant, 752.
precipitation of impurities in solution, 717, 718.
purification of solution: copper and cadmium precipitation, 717, 718.
importance, 718.
operation of tanks, 719.
slime treatment, 721.
zinc-dust precipitation, 717.
recovery, 713, 755.
recovery diagram, 713.
residue treatment, Great Falls plant, 735.
resistance of electrolyte: effect of acidity, 746, 747.
effect of temperature, 745, 746, 747.
roasting: experimental results, 85, 88, 89.
ferrite formation, 108, 706.
furnaces: Anaconda plant, 703, 707.
Great Falls plant, 703.
heat balance, 112, 125.
insoluble zinc compound formation, 108, 706.
Judge Mining & Smelting Co., 97, 112.
McDougall furnace results, 708.
reverberatory, 94.
sulfate, 105, 705, 709.
theory, 709.
Wedge furnaces, 96, 97, 708, 740, 741, 742.
scrap-iron precipitation of copper, 718.
solubility of zinc in sulfuric acid, 699.
sulfate roasting, 105, 705, 709.
Tainton-Pring process, 755.
time of cathode deposits, 701.
vs. electrothermal process, 123.
voltage: acidity effect, 750.

Electrolytic zinc: voltage: spacing of electrodes effect, 749, 750.
zinc-dust manufacture, 734.
zinc-dust precipitation, 717.
Electrolytic Zinc (HANSEN), 85; *Discussion:* (SCHOLL), 119, 123; (HANSEN), 120, 121, 122, 124, 127; (HAMILTON), 120; (RALSTON), 121, 124; (MATHEWSON), 122, 124; (LYON), 122; (RICHARDS), 123; (FULTON), 123, 124; (GUESS), 125.
Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont. (LAIST, FRICK, ELTON and CAPLES), 699; *Discussion:* (BULLOCK), 753; (SMITH), 754, 755, 756, 757; (BREYER), 755, 756; (READ), 756; (HEIMROD), 756; (OSTGREN), 756; (SEGUINE), 757; (HIXON), 757; (MATHEWSON), 757; (JORGENSEN), 757; (ELTON and CAPLES), 758.
Elongation: aluminum wire, 807, 810, 811, 812.
molybdenum wire, 800, 807, 808.
nickel wire, 794, 805.
ELTON, J. O. and CAPLES, R. B.: *Discussion on Electrolytic Zinc Plant of Anaconap Copper Mining Co. at Great Falls, Mont.*, 758.
ELTON, J. O., LAIST, FREDERICK, FRICK, F. F. and CAPLES, R. B.: *Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 699.
Embrittlement: copper, salt bath, 439, 463.
experimental, lead, 447.
Equi-cohesive temperature: metals, 326.
zinc, 328.
Equilibrium diagram: aluminum-copper alloys, 14, 62.
aluminum-magnesium alloys, 18, 62.
copper-tin alloys, 421.
nickel-chromium alloys, 559.
Etching, aluminum alloys, 25.
Eutectic formation, tin-lead alloys, 532.
Expansion: coefficient, nickel, 405, 406.
dental amalgams, 492.

Feathering, cupellation, 612.
Fineness test, foundry sand, 632.
FINKELDEY, W. H., TREWIN, C. S. and MATHEWSON, C. H.: *Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod*, 305.
FINN, A. N., MERICA, P. D. and WALTENBERG, R. G.: *Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum with Copper, Nickel and Manganese*, 29.
First Year of Leaching by the New Cornelia Copper Co. (TOBELMANN AND POTTER): *Discussion:* (MACKAY), 568; (AUSTIN), 583.
Five Foundry Tests of Zinc Bronzes (KARR), 378; *Discussion:* (CORSE), 385, 386; (KARR), 385; (BASSETT), 385; (MCKINNEY), 386.
Flotation: Consolidated Coppermines Co., 820.
tests, Minerals Separation machine, 825.
X-cake and xylidin, 824, 828.
Flow sheet: coal-pulverizing plant, Nevada Consolidated Copper Co., 620.
concentrator, Consolidated Coppermines Co., 817.
Consolidated Coppermines Co., new mill, 822.
electrolytic zinc process, Anaconda Copper Mining Co., 715, 720.
reclamation of metal from foundry refuse, 651, 652.
Flue-dust, analysis, Tooele smelter, 770.
Flue-type Cottrell treater, Tooele, 764.
Fluxes: chemical action, 668.
chlorides, 668.
classification, 662.
materials, 662.
physical action, 673.
Fluxing, foundry: ammonia deoxidation, 672.
chemistry, 663.
chloride fluxes, chemical action, 668.
deoxidizers, 670.
fluid covers, 670.
physical action, 673.
physical changes caused, 664.
surface films, 673.
viscosity effect, 664.

FORD, ALLEN P.: *Discussion on Tin Fusible Boiler-plug Manufacture and Testing*, 237.
Foundry fluxing, see *Fluxing, foundry.*
Foundry refuse, reclamation of metal, 650.
Foundry sands, see *Sands, foundry.*
Foundry slag, treatment for reclamation of metal, 650.
Foundry tests, zinc bronzes, 378.
Fracture: intercrystalline, 443.
nature, 443.
FRANK, W. K.: *Discussion on a New Process for Making Fifteen Per Cent. Phosphor-copper*, 487.
FREEMAN, J. R., WALTENBERG, R. G. and MERICA, P. D.: *Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium*, 3.
Freezing-point curve: antimony-tin alloys, 233, 237.
copper-tin alloys, 233.
lead-tin alloys, 234.
zinc-lead alloys, 234.
FRICK, F. F., LAIST, FREDERICK, ELTON, J. O. and CAPLES, R. B.: *Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 699.
Fuel, metallurgical, coke-oven products, 640.
FULTON, C. H.: *Electric-resistance Furnace of Large Capacity for Zinc Ores*, 188; *Discussion*, 224, 225, 226.
Discussion on Electrolytic Zinc, 123, 124.
Fume: assay muffle, 604.
cupel furnaces, 603.
drying of cement copper briquets, 83.
Furnace, electric, zinc distillation, 189, 190, 202, 205, 208, 209, 216, 217.
Fusible boiler-plugs, see *Boiler-plugs, fusible.*

Galvanic action due to size of electrodes, 462, 463.
Gas: coke-oven: analysis, 648.
use as metallurgical fuel, 644.
producer, from coke, 645.
Gases in molten copper and brass, 666.
GIBSON, W. A.: *Discussion on Heat Treatment of Aluminum-alloy Castings*, 290, 291, 292.
GIBSON, W. A. and JEFFRIES, ZAY: *Heat Treatment of Aluminum-alloy Castings*, 270.
Glue, electrolytic zinc, 728, 756, 757, 761.
Gold, volatilization in assaying, 601, 605.
Government bronze, 378.
Grain Growth in Alpha Brass (SMITH), 159; *Discussion:* (SMITH), 187.
Granular lead, 457.
GRAY, ARTHUR W.: *Transition Phenomena in Amalgams*, 488; *Discussion*, 505.
Great Falls, Mont., electrolytic zinc, 699.
GRUBB, A. A.: *Discussion on Laboratory Testing of Sands, Cores, and Core Binders*, 637, 638, 639.
GRUBB, A. A. and WOLF, F. L.: *Laboratory Testing of Sands, Cores and Core Binders*, 630.
GUESS, GEORGE A.: *Discussion on Electrolytic Zinc*, 125.
Gun metal: annealing, effect, 294.
heat treatment, tests, 293.
quenched, photomicrographs, 298, 303.
quenching, effect, 293.
GUREVICH, L. J. and HROMATKO, J. S.: *Tin Fusible Boiler-plug Manufacture and Testing*, 227.

HALL, F. A.: *Discussion on Intercrystalline Brittleness of Lead and Copper*, 460.
HAMILTON, E. H.: *Discussion on Electrolytic Zinc*, 120.
HANSEN, C. A.: *Electrolytic Zinc*, 85; *Discussion*, 120, 121, 122, 124, 127.
Hardening: aluminum alloys, 270.
duralumin, 41, 71, 270.
Hardness: aluminum-copper alloys, 474.
nickel, 412, 415.
rolled zinc, 352.
HART, LEON O.: *Nickel-chromium alloys*, 554.
Heat balance, Wedge roaster, zinc ores, 112, 125.

Heat treatment: aluminum-alloy castings, 270.
aluminum alloys, increase of tensile strength, 35.
bronze, 293.
duralumin, 43.
gun metal, tests, 293.
zinc bronze, effect, 380.
Heat Treatment and Constitution of Duralumin (MERICA, WALTENBERG and SCOTT), 41; *Discussion:* (JEFFRIES), 77; (MERICA), 79.
Heat Treatment of Aluminum-alloy Castings (JEFFRIES and GIBSON), 270; *Discussion:* (BURGESS), 289; (MERICA), 289, 290, 291; (GIBSON), 290, 291, 292; (KARR), 290; (RAWDON), 291; (MCCULLOCH), 291.
HEIMROD, A. A.: *Discussions: on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 756.
on Tooele Flue-type Cottrell Treater, 779.
HILL, C.W., THOMAS, T. B. and VIETZ, W. B.: *Investigation of Brass Foundry Fluxes*, 662.
HIXON, H. W.: *Discussions: on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 757.
on Steel Chimneys and their Linings in Copper Smelting Plants, 838.
Horwood process, objections for Butte ores, 699.
HROMATKO, J. S. and GUREVICH, L. J.: *Tin Fusible Boiler-plug Manufacture and Testing*, 227.
HULST, GEORGE P.: *Treating Antimony Ores*, 566.
Hydrogen: effect in copper, 461, 462.
evolution from molten copper and brass, 667.
Hydrogen-sulfide precipitation, copper leaching, 584.
Hydrometallurgy, copper, see *Leaching process, copper.*

Impact tests, Charpy, see *Charpy impact tests.*
Impurities: constantan, effect, 245.
effects on properties of molten and cast metal, 663.
effects, rolled zinc, 318.
electrolytic zinc, behavior, 111.
introduction in melting aluminum, 664, 665.
introduction in melting metal, 663.
manganin, effect, 265.
nickel, effect, 408.
tin boiler-plug filling, 232, 237.
Influence of Heat Treatment on Gun Metal (SMART), 293; *Discussion:* (WOOD), 300; (MCKINNEY), 301, 302; (CORSE), 302; (COMSTOCK), 302.
Institute of Metals Division: Columbus meeting, 1920, viii.
Philadelphia meeting, 1919, vii.
Intercrystalline brittleness: copper, 439.
high temperatures, 152.
lead, 443.
Intercrystalline Brittleness of Lead (RAWDON), 443; *Discussion:* (RICHARDS), 458, 460, 462, 463; (JEFFRIES), 459; (CLAMER), 460; (HALL), 460; (YENSEN), 461; (ANTISELL), 462; (PILLING), 463; (RAWDON), 465.
Intercrystalline fracture, 443.
International Lead Refining Co., antimony ore smelting, 566.
International Nickel Co.: constantan investigations, 239.
nickel, commercial forms, 391.
International Smelting Co., Tooele: Cottrell treater, 764.
flue-dust analysis, 770.
steel chimney, 834.
Inverse-rate method, thermal analysis, 26.
Investigation of Brass Foundry Fluxes (HILL, THOMAS and VIETZ), 662; *Discussion:* (THOMAS), 674; (ROAST), 675; (SCHÜTZ), 675; (BERRY), 675.
Iron: copper leaching: effect in electrolyte, 581.
precipitation, 574.
solution, 573.
effect in aluminum alloys, 277, 281.
Swedish, magnetic properties, 401.
Iron-carbon alloys: allotropic changes, 535.
colloidal theory, 536.
constituent forms, 537, 539.
Isocolloids, 525.

Jackson electrode cooler, 207.
JAMES, ALFRED: *John Stewart MacArthur, Biographical Sketch*, 840.
JEFFRIES, ZAY: *Discussions: on Colloidal State in Metals and Alloys*, 546.
on Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals, 814, 815.
on Heat Treatment and Constitution of Duralumin, 77.
on Intercrystalline Brittleness of Lead and Copper, 459.
JEFFRIES, ZAY and GIBSON, W. A.: *Heat Treatment of Aluminum-alloy Castings*, 270.
John Stewart MacArthur, Biographical Sketch (JAMES), 840.
JONES, J. L.: *Discussions: on Physical Properties of Nickel*, 417, 418.
on Reclamation of Metal from Brass-foundry Refuse, 659.
JORGENSEN, E. L.: *Discussion on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 757.
Judge Mining & Smelting Co., Wedge furnace roasting, 97, 112.

KARR, C. P.: *Five Foundry Tests of Zinc Bronzes*, 378; *Discussion*, 385.
Discussions: on Heat Treatment of Aluminum-alloy Castings, 290.
on Physical Properties of Certain Lead-zinc Bronzes, 430, 431.
KARR, C. P. and STALEY, HOMER F.: *Physical Properties of Certain Lead-zinc Bronzes*, 420
KELLER, EDWARD: *Water and Chlorides in Cement Copper Briquettes*, 80.
Kromore, 564.
KRYNITZKY, A. I. and RAWDON, HENRY S.: *Deterioration of Nickel Spark-plug Terminals in Service*, 129.
KUZELL, C. R.: *Discussion on Steel Chimneys and their Linings in Copper Smelting Plants*, 836.

Laboratory Testing of Sands, Cores, and Core Binders (WOLF and GRUBB), 630; *Discussion:* (GRUBB), 637, 638, 639; (SCHUTZ), 638; (LANE), 638; (SLEETH), 638; (CLAMER), 638.
LAIST, FREDERICK and MAGUIRE, H. J.: *Reverberatory Furnace for Treating Converter Slag at Anaconda*, 585.
LAIST, FREDERICK, FRICK, F. F., ELTON, J. O. and CAPLES, R. B.: *Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 699.
LANE, A. C.: *Discussion on Laboratory Testing of Sands, Cores, and Core Binders*, 638.
LANGDON, S. C. and RAWDON, HENRY S.: *A Peculiar Type of Intercrystalline Brittleness of Copper*, 439.
Latent heat, nickel, 399.
Leaching, zinc ore, see *Electrolytic zinc, leaching.*
Leaching process, copper: accumulation of aluminum and iron in solution, 573.
acid strength of solvent, 572.
analysis of ore, 569.
chemical control: acid strength, 572.
requirements, 569.
crushing fineness, 570.
electrolyte analyses, 578.
electrolytic deposition, 578.
hydrogen-sulfide precipitation, 584.
iron in electrolyte, effect, 581.
leaching methods, 575.
New Cornelia Copper Co.: modifications suggested, 580.
ore characteristics, 570.
power saving, possible, 580.
solution of copper and impurities, 571.
ore preparation, 569.
precipitation of aluminum and iron oxides in solution, 574.
precipitation of copper, 584.
selective solution, 571.
sulfate formation, selective, 571.
Utah Copper Co., 584.
wash-water analysis, 576.
washing, 576.
Lead: allotropism, 447.
antimonial, International Lead Refining Co., 566.
brittle, properties, 445.
brittleness, intercrystalline, 443.

Lead: corroded, photomicrographs, 445.
effect in nickel-silver sheets, 511, 523.
effect of nitric-acid solution of lead acetate, 448, 449, 454.
embrittled, photomicrographs, 444, 450.
embrittlement, experimental, 447.
granular condition, 457.
volatilization, 610.
Lead cathode: attack in alkaline solution, 458.
nitric-acid electrolyte, 453, 455.
Lead sheathing, corroded, 443.
Lead-tin alloys: colloidal state, 532.
freezing-point curve, 234.
Lead-zinc alloys, freezing-point curve, 234.
Lead-zinc bronzes: photomicrographs, 422.
physical properties, 420, 427.
test bars, preparation, 425.
Le Chatelier, H.: *Discussion on Colloidal State in Metals and Alloys*, 547.
Lining, steel chimneys, 831.
Linton, Robert: *Treatment Tests on Ores of Consolidated Coppermines Co.*, 816.
Lynite Laboratories, Charpy impact tests, aluminum alloys, 466.
Lyon, Dorsey A.: *Discussion on Electrolytic Zinc*, 122.

McCulloch, Leon: *Discussion on Heat Treatment of Aluminum-alloy Castings*, 291.
McDougall furnace: chloridizing roasting, silver-tin ores, 680.
roasting, zinc concentrates, Anaconda, 708.
McGregor, A. G.: *Steel Chimneys and their Linings in Copper Smelting Plants*, 830; *Discussion*, 839.
McKinney, P. E.: *Discussions: on Five Foundry Tests of Zinc Bronzes*, 386.
on Influence of Heat Treatment on Gun Metal, 301, 302.
on Physical Properties of Certain Lead-zinc Bronzes, 430.
MacArthur, John Stewart, biographical sketch, 840.
Mackay, Henry S.: *Chemical and Electrochemical Problems Involved in New Cornelia Copper Co.'s Leaching Process*, 568.
MacPherran, R. S.: *Discussion on Physical Properties of Nickel*, 418.
Macrographs, brass, structure after annealing, 160.
Magnesium: effect in aluminum alloys, 277, 278, 281.
effect in duralumin, 72.
effect on solubility of $CuAl_2$ in aluminum, 15.
Magnesium-aluminum alloys: equilibrium, 15, 18.
equilibrium diagram, 62.
photomicrographs, 16.
Magnesium-aluminum-nickel alloys, mechanical properties, 34.
Magnesium-copper-aluminum alloys, mechanical properties, 33.
Magnesium-manganese-aluminum alloys, mechanical properties, 32.
Magnetic properties: iron, Swedish, 401.
nickel, 400.
Magnetite, reverberatory slags, 596, 597, 598, 599.
Maguire, H. J. and Laist, Frederick: *Reverberatory Furnace for Treating Converter Slag at Anaconda*, 585.
Maier, C. G.: *Discussion on Reverberatory Furnace for Treating Converter Slag at Anaconda*, 597, 600.
Manganese: effect in electrolytic zinc process, 701, 729, 730.
effect in nickel, 410.
effect on e.m.f. of copper-nickel alloy against iron, 245.
Manganese-magnesium-aluminum alloys, mechanical properties, 32.
Manganin: annealing, 262.
composition, 262.
impurities, effect, 265.
manufacture, 261.
melting, 263.
properties, 261.
resistance measuring material, 266.
temperature coefficients, 266.
Manufacture: boiler-plugs, fusible, 227, 235.
constantan, 239.
manganin, 261.

Manufacture and Electrical Properties of Constantan (BASH), 239.
Manufacture and Electrical Properties of Manganin (BASH), 261; *Discussion:* (WENNER), 266; (SMITH), 268; (BASH), 268, 269; (DRIVER), 269; (BASSETT), 269.
Marten's tests, rolled zinc, 312.
Martensite, 538.
Martinez, Calif., electrolytic zinc, 755.
MATHEWSON, C. H.: *Discussion on Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod*, 377.
MATHEWSON, C. H., TREWIN, C. S. and FINKELDEY, W. H.: *Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod*, 305.
MATHEWSON, E. P.: *Discussions: on Electrolytic Zinc*, 122, 124.
on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont., 757.
on Reverberatory Furnace for Treating Converter Slag at Anaconda, 596, 598, 599.
Mechanical properties: aluminum-copper alloys, 474.
aluminum-magnesium-copper alloys, 33.
aluminum-magnesium-manganese alloys, 32.
aluminum-magnesium-nickel alloys, 34.
aluminum wire, 806.
metals: effect of temperature, etc., tests, 781.
rate of loading effect, 809.
molybdenum wire, 792, 797.
nickel wire, 131, 789.
Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum and Magnesium with Copper, Nickel, and Manganese (MERICA, WALTENBERG, and FINN), 29; *Discussion:* (BURGESS), 40.
Mechanical tests: gun metal, heat treated, 297.
nickel silver sheets, 510.
Melting: constantan, 251.
manganin, 263.
metal: borax cover, 670, 675.
fluid covers, 670.
impurities introduced, 663.
surface films, 673.
zinc cathodes, 732.
Melting points: chlorides, 83.
nickel-chromium alloys, 563.
MERICA, PAUL D.: *Simplification of Inverse-rate Method for Thermal Analysis*, 26.
Discussions: on Charpy Impact Test as Applied to Aluminum Alloys, 481.
on Colloidal State in Metals and Alloys, 544.
on Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium, 25.
on Deterioration of Nickel Spark-plug Terminals in Service, 157.
on Heat Treatment and Constitution of Duralumin, 79.
on Heat Treatment of Aluminum-alloy Castings, 289, 290, 291.
MERICA, P. D., WALTENBERG, R. G. and FINN, A. N.: *Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum with Copper, Nickel and Manganese*, 29.
MERICA, P. D., WALTENBERG, R. G. and FREEMAN, J. R.: *Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium*, 3.
MERICA, P. D., WALTENBERG, R. G. and SCOTT, H.: *Heat Treatment and Constitution of Duralumin*, 41.
Merton furnace: chloridizing roasting of silver-tin ores, 684.
modified, 686.
Metal, molten, viscosity, 664.
Metal reclamation, foundry refuse, 650.
Metallography, limitations, 544.
Metallurgy, nickel, 388.
Meyer's tests, rolled zinc, 313, 315.
Microstructure: duralumin, 65.
nickel, 415.
nickel silver sheets, 515.
nickel wire, 132.
Milling, copper ore, Consolidated Coppermines Co., 816.
Minerals Separation machine, flotation tests, 825.

Mist, cell rooms, electrolytic zinc, 756, 761.
Molecular forces, metals, effect of change on physical properties, 525.
Molybdenum, photomicrographs, temperature tests, 784, 785, 786.
Molybdenum wire: elongation, 800, 807, 808.
mechanical properties, at various temperatures, 792.
reduction of area, 802, 808, 809.
tensile strength, 797, 806, 807.
Mond process, 390.
Moore's tests, rolled zinc, 316.
MOUSSETTE, O. J.: *Discussion on Reclamation of Metal from Brass-foundry Refuse*, 661.

Nevada Consolidated Copper Co., pulverized-coal plant, 618.
New Cornelia Copper Co., leaching, copper, see *Leaching process, copper.*
New Process for Making Fifteen Per Cent. Phosphor-copper (DEMMLER), 483; *Discussion:* (DEMMLER), 486, 487; (FRANK), 487; (CLAMER), 487.
Nichrome: analysis, 559.
properties, 558, 561.
Nichrome II, properties, 562.
Nickel: analysis, 391, 392, 394.
annealing, 414, 417.
atomic weight, 393.
carbon content, effect, 408.
chemical method of production, 388.
commercial, 388.
conductivity, thermal, 399.
decoloring power, 408.
effect in bronze, 430.
electrolytic, 391.
expansion, coefficient, 405, 406.
forms: commercial, 388.
International Nickel Co., 391.
grade D, 392.
hardness, 412, 415.
impurities, effect, 408.
latent heats, 399.
magnetic properties, 400.
malleable, 392, 413.
melting point, 397.
metallurgy, 388.
microstructure, 415.
Mond process, 390.
occlusion of gases, 405, 407.
Orford process, 390.
photomicrographs, 416, 783, 784.
physical properties, 387.
pickling, 414.
production processes, 388.
resistivity, electrical, 403.
rolled, properties, 414.
sheet: photomicrographs, 157.
tensile properties, 417.
shot, 391.
shrinkage, 413.
specific gravity, 393, 396.
specific heat, 397.
tensile properties, 411, 415, 417.
transformation point, 397.
variability, 387.
welding properties, 412.
wet method of production, 388.
working, 413.
Nickel-chromium alloys: freezing-point diagram, 559.
iron free, 562.
Kromore, 564.
melting points, 563.
thermo-electromotive force, 560, 563.

Nickel-chromium Alloys (HART), 554.
Nickel-chromium-iron alloys: resistances and temperature, 556.
resistivity, 554.
temperature coefficient, 555.
thermo-electromotive force, 557.
Nickel-chromium steel: resistivity, 554.
temperature coefficient, 555.
types, 554.
Nickel-copper alloys, thermo-electromotive force against iron, 243.
Nickel-magnesium-aluminum alloys, mechanical properties, 34.
Nickel silver, analysis, 510.
Nickel silver sheets: annealed, tests, 513, 519.
cold-rolled, tests, 512.
lead content, effect, 511, 523.
microstructure, 515.
photomicrographs, 514, 517.
tests: analysis, 510.
annealed strips, 511.
methods, 511.
rolled specimens, 511, 516.
Nickel spark-plug terminals: composition, 129, 143.
deterioration: brittleness at high temperature, 152.
contributing factors, 143.
explanation, 154.
intense local heating, 149.
macroscopic properties, 129.
microstructural features, 132.
oxidation, 143.
photomicrographs, 133.
reducing atmosphere, 147, 148.
stress and heat combined effect, 150, 151.
transverse cracks, 135, 138.
Nickel wire: see also *Nickel spark-plug terminals.*
elongation, 794, 805.
mechanical properties, at various temperatures, 788, 804.
reduction of area, 792.
tensile strength, 789, 804.

Occlusion of gases, nickel, 405, 407.
Ohio Brass Co.: foundry sand testing, 630.
reclaiming plant, foundry refuse, 650.
Orford process, 390.
OSTGREN, G. L.: *Discussion on Electrical Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 756.
Oxidation: nickel spark-plug terminals, 143.
silver, 609.
Oxygen, effect in copper, 433, 435.

Peculiar Type of Intercrystalline Brittleness of Copper (RAWDON and LANGDON), 439; *Discussion:* (RICHARDS), 458, 460, 462, 463; (JEFFRIES), 459; (CLAMER), 460; (HALL), 460; (YENSEN), 461; (ANTISELL), 462; (PILLING), 463; (RAWDON), 465.
Permeability test, foundry sand, 632.
PETERS, CHAUNCEY and SOUDER, WILMER: *Discussion on Transition Phenomena in Amalgams*, 501.
Philadelphia meeting, 1919, vii.
Phosphor-copper: grades, 483.
new process, 483.
processes of making, 483.
Phosphorization of copper, 484.
Phosphor-tin, manufacture, 487.
Photomicrograph: aluminum, commercial, 5.
aluminum-alloy castings, 285.
aluminum-copper alloys, 10, 12.

Photomicrograph: boiler-plugs, tin, casing and filling, 229.
brass, annealed, 168.
constantan, 248.
copper, embrittled, 440, 464.
duralumin, 67.
gun metal, quenched, 298, 303.
lead: corroded, 445.
embrittled, 444, 450.
lead cathode, nitric-acid electrolyte, 455.
magnesium-aluminum alloys, 16.
molybdenum, temperature tests, 784, 785, 786.
nickel: rolled, 416.
temperature tests, 783, 784.
nickel sheet, 157.
nickel silver sheets: annealed, 517.
cold-rolled, 514.
nickel wire used for spark-plug terminals, 133.
zinc, rolled, 338.
zinc bronze, 422.
Physical properties: see also *Mechanical properties* and *Tensile properties*.
coke, byproduct, 647.
copper, 432.
lead-zinc bronzes, 420, 427.
metals: effect of changes in molecular forces, 525.
effect of rapid chilling, 526.
nichrome, 558, 561.
nickel, 387.
zinc bronze, 379.
Physical Properties of Certain Lead-zinc Bronzes (STALEY and KARR), 420; *Discussion:* (CORSE), 430; (KARR), 430, 431; (MCKINNEY), 430; (WOOD), 431.
Physical Properties of Nickel (BROWNE and THOMPSON), 387; *Discussion:* (PRICE and DAVIDSON), 414; (JONES), 417, 418; (THOMPSON), 417, 418, 419; (MACPHERRAN), 418; (BASSETT), 418; (PRICE), 419.
Physical Tests on Sheet Nickel Silver (PRICE and DAVIDSON), 510; *Discussion:* (WEBSTER), 523; (DAVIDSON), 523.
PILLING, N. B.: *Discussion on Intercrystalline Brittleness of Lead and Copper*, 463.
Pitch, coke-oven: properties, 648.
viscosity, 641.
Pitch, copper refining, 432.
POMEROY, R. E. H.: *Coal-pulverizing Plant at Nevada Consolidated Copper Smelter*, 618; *Discussion*, 628.
PORTH, W. H.: *Discussion on Some Applications of Rolled Zinc Strip and Drawn Zinc Rod*, 376, 377.
Potash recovery, Cottrell precipitation, cement plant, 777.
Potter, James A. and Tobelmann, Henry A., 568 et seq.
Power: cost, electrolytic zinc, effect of acidity of solution, 751.
distribution, electrolytic zinc, Great Falls plant, 752.
efficiency, electrolytic zinc, 748.
Precipitation characteristics, dust and fume, 772.
Precipitation of impurities, electrolytic zinc process, 717, 718.
PRICE, W. B.: *Discussion on Physical Properties of Nickel*, 419.
PRICE, W. B. and DAVIDSON, PHILIP: *Physical Tests on Sheet Nickel Silver*, 510.
Discussion on Physical Properties of Nickel, 414.
Producer gas: coke as source, 645.
from coke, properties, 649.
Pulverized coal: advantages, 618.
Bonnet pulverizer, 623.
distributing fans, 625.
dryers, Ruggles-Coles, 621.
flow sheet, Nevada Consolidated Copper Co., 620.
Nevada Consolidated Copper Co., 618.
PYNE, F. R.: *Discussion on Relationship of Physical and Chemical Properties of Copper*, 438.

Quenching: gun metal, effect, 293.
water, aluminum-alloy castings, 271.

RALSTON, O. C.: *Discussion on Electrolytic Zinc*, 121, 124.
Rate of loading, effect on mechanical properties of metals, 809.
RAWDON, HENRY S.: *Intercrystalline Brittleness of Lead*, 443; *Discussion*, 465.
Discussions: on Heat Treatment of Aluminum-alloy Castings, 291.
on Intercrystalline Brittleness of Lead and Copper, 465.
RAWDON, HENRY S. and KRYNITZKY, A. I.: *Deterioration of Nickel Spark-plug Terminals in Service*, 129.
RAWDON, HENRY S. and LANGDON, S. C.: *A Peculiar Type of Intercrystalline Brittleness of Copper*, 439.
READ, T. T.: *Discussion on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 756.
Reclaiming plant, foundry refuse, Ohio Brass Co., 650.
Reclamation of metal from foundry refuse: analyses, 654.
concentration, 652, 659, 660, 661.
costs, 655.
flow sheets, 651, 652.
preliminary treatment, 650.
representative run, 656.
slag treatment, 650.
sweepings treatment, 651.
Reclamation of Metal from Brass-foundry Refuse (WOLF and ALDERSON), 650; *Discussion:* (JONES), 659; (ALDERSON), 660, 661; (CLAMER), 660; (THUM), 660; (MOUSSETTE),661.
Reduction of area: aluminum wire, 808, 811.
molybdenum wire, 802, 808, 809.
Refuse, foundry, reclamation of metal, 650.
Relationship of Physical and Chemical Properties of Copper (ANTISELL), 432; *Discussion:* (BASSETT), 436; (CAESAR), 436; (WEBSTER), 437, 438; (WALKER), 437, 438; (PYNE), 438.
Remelting, effect, zinc bronze, 382.
Residue treatment, electrolytic zinc, 735.
Resistance, electrolyte, zinc: acidity effect, 746, 747.
temperature effect, 745, 746, 747.
Resistance materials, standard, 266.
Resistance-temperature coefficient, manganin, 266.
Resistance to corrosion, aluminum alloys, rolled, 36.
Resistivity, electrical: chromium alloys, 561.
duralumin, 59, 60.
nickel-chromium-iron alloys, 554.
nickel, 403.
zinc-ore briquets, 200, 201.
Reverberatory furnace, straight-line, chloridizing roasting, 683.
Reverberatory Furnace for Treating Converter Slag at Anaconda (LAIST and MAGUIRE), 585; *Discussion:* (MATHEWSON), 596, 598, 599; (SMITH), 596, 599; (MAIER) 597, 600; (THUM), 597, 598; (ROBIE), 598.
Reverberatory furnace gases, steel chimneys, 831, 835.
Reverberatory slag: copper content, form, 597.
magnetite content, 596, 597, 598, 599.
Reverberatory smelting: Anaconda, 585.
converter slag: analyses, 593.
equipment, 587.
experimental data, 586.
furnace, 587.
operation, 590.
results, 591.
RICHARDS, J. W.: *Discussions: on Electric-resistance Furnace of Large Capacity for Zinc Ores*, 224, 225, 226.
on Electrolytic Zinc, 123.
on Intercrystalline Brittleness of Lead and Copper, 458, 460, 462, 463.
on Volatilization in Assaying, 616.
Riverside Portland Cement Co., Cottrell treater, 775.
ROAST, H. J.: *Discussion on Investigation of Brass Foundry Fluxes*, 675.
Roaster gases, steel chimneys, 831.
Roasting, zinc ore: electrically heated furnace, 89.
for electrolytic process, see *Electrolytic zinc, roasting.*

Roasting and Chloridizing of Bolivian Silver-tin Ores (SÖHNLEIN), 676; *Discussion:* (BLIEK), 694.
Roberts-Austen method, modified, thermal analysis, dental amalgams, 497.
ROBIE, E. H.: *Discussions: on Reverberatory Furnace for Treating Converter Slag at Anaconda*, 598.
on Steel Chimneys and their Linings in Copper Smelting Plants, 838.
Rolled zinc, see *Zinc, rolled.*
Ruggles-Coles dryers, pulverized coal, 621.
RULE, Y. A.: *Discussion on Tooele Flue-type Cottrell Treater*, 777.
RUTHERFORD, FOREST: *Discussion on Steel Chimneys and their Linings in Copper Smelting Plants*, 837.

Sands, foundry, testing: composition, 631.
fineness, 632.
gas content, 635.
Ohio Brass Co., 630.
permeability, 632.
strength, 636.
SCHOLL, G. D.: *Discussion on Electrolytic Zinc*, 119, 123.
SCHUTZ, F. A.: *Discussions: on Investigation of Brass Foundry Fluxes*, 675.
on Laboratory Testing of Sands, Cores, and Core Binders, 638.
SCOTT, H., MERICA, P. D. and WALTENBERG, R. G.: *Heat Treatment and Constitution of Duralumin*, 41.
SEGUINE, W.: *Discussion on Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.*, 757.
Set, copper refining, 432.
Sheet nickel, tensile properties, 417.
Sheets, nickel silver, see *Nickel silver sheets.*
Silicon, effect in commercial aluminum, 7.
SILSBEE, FRANCIS B.: *Discussion on Deterioration of Nickel Spark-plug Terminals in Service*, 156.
Silver: oxidation, 609.
spitting, 610.
volatilization in assaying, 601, 607.
Silver-tin ores, Bolivian: amalgamation, 677.
chloridizing: Cottrell precipitation of dust, 681.
dust losses, 681.
dust treatment, 682.
early methods, 678.
efficiency of modified Merton furnace, 688.
hand-rabbled furnace, 678.
intermittent system, advantages, 688, 691.
Machacamarca mechanical furnace, 680.
McDougall furnace, 680.
mechanical furnace, first, 680.
Merton furnace, 684.
Söhnlein furnace, 686, 696.
straight-line furnace, 683.
volatilization losses, 681.
composition, 676.
crushing for chloridizing, 693.
cyaniding experiments, 677.
early treatment, 676.
roasting, Huanchaca ore, 679.
Simplification of Inverse-rate Method for Thermal Analysis (MERICA), 26.
Slag: converter, see *Converter slag.*
foundry, reclamation of metal, 650.
SLEETH, H. B.: *Discussion on Laboratory Testing of Sands, Cores, and Core Binders*, 638.
SMART, C. F.: *Influence of Heat Treatment on Gun Metal*, 293.
Smelting: antimony, International Lead Refining Co., 566.
reverberatory, see *Reverberatory smelting.*
SMITH, F. G.: *Grain Growth in Alpha Brass*, 159; *Discussion*, 187.
Discussion on Manufacture and Electrical Properties of Manganin, 268.

SMITH, W. C.: *Discussions: on Electrolytic Zinc Plant of Anaconda Copper Mining Co., at Great Falls, Mont.*, 754, 755, 756, 757.
on Reverberatory Furnace for Treating Converter Slag at Anaconda, 596, 599.
Sodium chloride, action in melting copper, 80.
Söhnlein furnace, chloridizing, 686, 696.
SÖHNLEIN, M. G. F.: *Roasting and Chloridizing of Bolivian Silver-tin Ores*, 676.
Solubility: $CuAl_2$ in aluminum at different temperatures, 9, 14.
$FeAl_3$ in aluminum, 9.
metals and compounds in aluminum, 20.
Mg_4Al_3 in aluminum, 15.
Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod (MATHEWSON, TREWIN, and FINKELDEY), 305; *Discussion:* (PORTH), 376, 377; (MATHEWSON), 377; (BREYER), 377.
Sorbite, 538.
SOUDER, WILMER and PETERS, CHAUNCEY: *Discussion on Transition Phenomena in Amalgams*, 501.
Spark-plug terminals, nickel, see *Nickel spark-plug terminals.*
Specific gravity, nickel, 393, 396.
Specific heat: metals, 398.
nickel, 397.
Specifications: boiler-plugs, fusible, 227, 228.
constantan, 239.
copper, 432.
SPERR, F. W., JR.: *Coke and Byproducts as Fuels for Metals Melting*, 640.
Spitting, silver, 610.
Stacks, see *Chimneys.*
STALEY, HOMER F. and KARR, C. P.: *Physical Properties of Certain Lead-zinc Bronzes*, 420.
Steamboat Inspection Service, boiler-plug specifications, 227, 228.
Steel: colloidal theory, see *Iron-carbon alloys.*
constituent forms, 537, 539.
Steel chimneys, see *Chimneys, steel.*
Steel Chimneys and their Linings in Copper Smelting Plants (MCGREGOR), 830; *Discussion:* (KUZELL), 836; (THUM), 836; (RUTHERFORD), 837; (HIXON), 838; (ROBIE), 838; (MCGREGOR), 839.
Steptoe Reduction Works, concentration, 817.
Stiffness, worked zinc, 367.
Stop-watch, use in thermal analysis, 27.
Straight-line furnace, chloridizing roasting, 683.
Sulfate formation, copper leaching, selective, 571.
Sulfate roasting, electrolytic zinc, 105, 705, 709.
Supercooled melts, factors controlling behavior, 527.
Surface tension, energy accumulation in colloidal state, 547.
Swedish iron, magnetic properties, 401.
Sweepings, foundry, reclamation of metal, 651.
SYKES, W. P.: *Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals*, 780; *Discussion*, 815.

Tainton-Pring process, electrolytic zinc, 755.
Tar, coke-oven: properties, 648.
use as metallurgical fuel, 643.
viscosity, 641.
Temperature coefficient: chromium alloys, 564.
nickel-chromium-iron alloys, 555.
Temperature coefficients of resistance, manganin, 266.
Temperature effect, mechanical properties: aluminum wire, 799.
molybdenum wire, 792.
nickel wire, 788, 804.
Tensile strength: aluminum alloys, increase by heat treatment, 35.
aluminum wire, 806, 809, 810, 812.
molybdenum wire, 797, 806, 807.
nickel, 411, 415, 417.
nickel wire, 789, 804.
zinc, rolled, 309, 315, 324, 346.
Tensile tests: aluminum-alloy castings, heat treated, 272.
elevated temperatures, zinc, 332.

Test bars: bronze, preparation, 425.
type, zinc bronze, 384.
Tests: bending: aluminum, 475.
aluminum alloys, 469, 472, 476, 479.
Charpy impact, see *Charpy impact test.*
cores and core binders, 630.
foundry, zinc bronzes, 378.
mechanical, see Mechanical tests.
mechanical properties of metals, effect of temperature, etc., 781.
physical: lead-wire bronzes, 427.
zinc bronze, 379.
sands, foundry, 630.
zinc, rolled, 309, 315, 324, 346.
Thermal analysis: dental amalgams, 488.
dilatometric method, 488.
inverse-rate method: use of chronograph, 26, 27.
use of stop-watch, 27.
Roberts-Austen method, modified, 497.
Thermocouples, iron-constantan, 239.
Thermo-electromotive force: copper-nickel alloys against iron, 243.
nickel-chromium alloys, 560, 563.
nickel-chromium-iron alloys, 557.
zinc alloys, 504.
THOMAS, T. B.: *Discussion on Investigation of Brass Foundry Fluxes*, 674.
THOMAS, T. B., HILL, C. W. and VIETZ, W. B.: *Investigation of Brass Foundry Flux*, 662.
THOMPSON, J. F.: *Discussion on Physical Properties of Nickel*, 417, 418, 419.
THOMPSON, J. F. and BROWNE, DAVID H.: *Physical Properties of Nickel*, 387.
THUM, E. E.: *Discussions: on Colloidal State in Metals and Alloys*, 544.
on Reclamation of Metal from Brass-foundry Refuse, 660.
on Reverberatory Furnace for Treating Converter Slag at Anaconda, 597, 598.
on Steel Chimneys and their Linings in Copper Smelting Plants, 836.
TILLSON, B. F.: *Discussion on Coal-pulverizing plant at Nevada Consolidated Copper Smelter*, 628.
Timofeeff's studies, rolled zinc, 316.
Tin-antimony alloys, freezing-point curve, 233, 237.
Tin boiler-plug filling, impurities, 232, 237.
Tin-copper alloys: equilibrium diagram, 421.
freezing-point curve, 233.
Tin Fusible Boiler-plug Manufacture and Testing (GUREVICH and HROMATKO), 227
Discussion: (COWAN), 236; (FORD), 237.
Tin-lead alloys: colloidal state, 532.
freezing-point curve, 234.
Tin-silver ores, see *Silver-tin ores.*
Tobelmann, Henry A. and Potter, James A., 568 et seq.
Tooele Flue-type Cottrell Treater (YOUNG), 764; *Discussion:* (WELCH), 771; (RULE), 777; (HEIMROD), 779.
Transformation point, nickel, 397.
Transition Phenomena in Amalgams (GRAY), 488; *Discussion:* (SOUDER and PETERS), 501; (GRAY), 505.
Treating Antimony Ores (HULST), 566.
Treatment Tests on Ores of Consolidated Coppermines Co. (LINTON), 816; *Discussion:* (CALLOW), 828.
TREWIN, C. S., MATHEWSON, C. H. and FINKELDEY, W. H.: *Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod*, 305.
Troostite, 538.
TUCKER, A. W.: *Discussion on Electric-resistance Furnace of Large Capacity for Zinc Ores*, 224.

Uses, zinc, rolled, 370.
Utah Copper Co., leaching process, 584.

VIETZ, W. B., HILL, C. W. and THOMAS, T. B.: *Investigation of Brass Foundry Fluxes*, 662.
Viscosity: coke-oven tar and pitch. 641.
molten metals, 664.

Volatilization: assaying: complexity, 601.
cupelling, 601, 602.
determination of amount, 614.
dusting loss, 603.
effect of other metals, 612.
evidence lacking, 601.
feathering, 612.
lead, 610.
muffle fume data, 604.
silver and oxygen relations, 609.
chlorides, 83.
cupel furnaces, fume data, 603.
gold, 601, 605.
lead, 610.
losses, chloridizing, silver-tin ores, 681.
relation to melting and boiling points, 604, 617.
silver, 601, 605.
Volatilization in Assaying (DEWEY), 601; *Discussion:* (RICHARDS), 616; (DEWEY), 617.

WALKER, A. L.: *Discussion on Relationship of Physical and Chemical Properties of Copper*, 437, 438.
WALTENBERG, R. G., MERICA, P. D. and FINN, A. N.: *Mechanical Properties and Resistance to Corrosion of Rolled Light Alloys of Aluminum with Copper, Nickel and Manganese*, 29.
WALTENBERG, R. G., MERICA, P. D. and FREEMAN, J. R.: *Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium*, 3.
WALTENBERG, R. G., MERICA, P. D. and SCOTT, H.: *Heat Treatment and Constitution of Duralumin*, 41.
Water and Chlorides in Cement Copper Briquettes (KELLER), 80.
WEBSTER, W. R.: *Discussions: on Physical Tests on Sheet Nickel Silver*, 523.
on Relationship of Physical and Chemical Properties of Copper, 437, 438.
Wedge furnace, roasting: heat balance, 112, 125.
zinc ores, 96, 97, 708.
WELCH, H. V.: *Discussion on Tooele Flue-type Cottrell Treater*, 771.
Welding properties, nickel, 412.
WENNER, F.: *Discussion on Manufacture and Electrical Properties of Manganin*, 266.
WILSON, A. B. and COMSTOCK, G. F.: *Discussion on Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium*, 21.
Wire: aluminum, see *Aluminum wire.*
constantan: analysis, 258.
tests, 257.
molybdenum, see *Molybdenum wire.*
nickel, see *Nickel wire.*
WOLF, F. L. and ALDERSON, G. E.: *Reclamation of Metal from Brass-foundry Refuse*, 650.
WOLF, F. L. and GRUBB, A. A.: *Laboratory Testing of Sands, Cores, and Core Binders*, 630.
WOOD, R. F.: *Discussions: on Influence of Heat Treatment on Gun Metal*, 300.
on Physical Properties of Certain Lead-zinc Bronzes, 431.
Worked zinc, see *Zinc, rolled.*

X-cake and xylidin, 824, 828.

YENSEN, T. D.: *Discussion on Intercrystalline Brittleness of Lead and Copper*, 461.
YOUNG, A. B.: *Tooele Flue-type Cottrell Treater*, 764.

Zinc: amorphous theory applications, 325.
dental amalgam constituent, 488, 504.
distillation, electric: briquets, 188, 191, 192, 196, 199.
coal in briquets, 198.
coke content of briquets, 193, 194, 195.
East St. Louis plant, 201.
electrical records, 213.
experimental work, 190.

Zinc: distillation, electric: furnace, 189, 190, 202, 205, 208, 209, 216, 217.
heat capacity of retort, 215, 216.
metal balance, 211.
pitch content of briquets, 193, 196.
power consumption, 222.
preheated retorts, 219, 221.
process, 188, 190.
size of ore and coke particles, 194.
vs. electrolytic, 123.
wiring diagram, 219.
zinc dust production, 223.
drawing, effect of speed on ductility, 361.
ductility: dynamic, 359.
rolled zinc, 359.
electrolytic, see *Electrolytic zinc.*
electrothermal vs. electrolytic processes, 123.
equi-cohesive temperature, 326, 328.
extruded, properties, 322.
Horwood process, objections for Butte ores, 699.
roasting: Anaconda electrolytic process, 703.
electrically heated furnace, 89.
experimental results, 88, 89.
heat balance, 112, 125.
reverberatory furnace, 94.
Wedge furnaces, 96, 97, 112.
rod and wire, 375, 376.
rolled: aluminum content, effect, 319.
annealing, 314, 341, 347, 352, 356.
applications, successful, 370.
bending properties, 354.
cold-bend values, 354.
copper content, effect, 321, 322.
ductility: at various temperatures, 334.
effect of annealing, 356.
effect of drawing speed, 361.
static and dynamic tests, 363.
grain refining, 339, 344, 345.
grain structure, 317, 336, 338, 344, 345.
hard- and soft-rolled, 340.
hardness, effect of annealing, 347, 352.
impurities, effects, 318.
literature, 307.
Martens' tests, 308, 312.
Meyer's tests, 313, 315.
Moore's tests, 316.
photomicrographs, 338.
rolling variables, effect, 335.
stiffness, 367.
stress-strain data, 309, 315, 324.
structural types, 336, 338.
tensile data at elevated temperatures, 332.
tensile strength, 309, 315, 324, 346.
tensile tests: effect of elevated temperatures, 312.
effect of interruption, 310.
effect of rate of loading, 310.
Timofeeff's studies, 316.
uses, 370.
roofing material, 372.
solubility in sulfuric acid, 699.
worked, see *Zinc, rolled.*
Zinc alloys, thermo-electromotive force, 504.
Zinc-aluminum alloys, 320.
inc bronze: heat-treatment effect, 380.
photomicrographs, 422.
physical properties, 379.
remelting effect, 382.

Zinc bronze: test bars, 384.
tests, physical, 379.
Zinc concentrates, roasting, Anaconda and Great Falls, 708.
Zinc dust: electric distillation, 223.
manufacture, Great Falls plant, 734.
precipitation of copper and cadmium in electrolytic zinc process, 717
Zinc ferrite, formation in roasting, 108.
Zinc-lead alloys, freezing-point curve, 234.
Zinc ore: Butte, treatment possibilities, 699.
leaching, see *Electrolytic zinc, leaching.*
Zinc rod, stress-deformation curves, pure and alloyed, 368.
Zinc strip, see *Zinc, rolled.*
Zinc sulfate, decomposition pressure, 107, 108.

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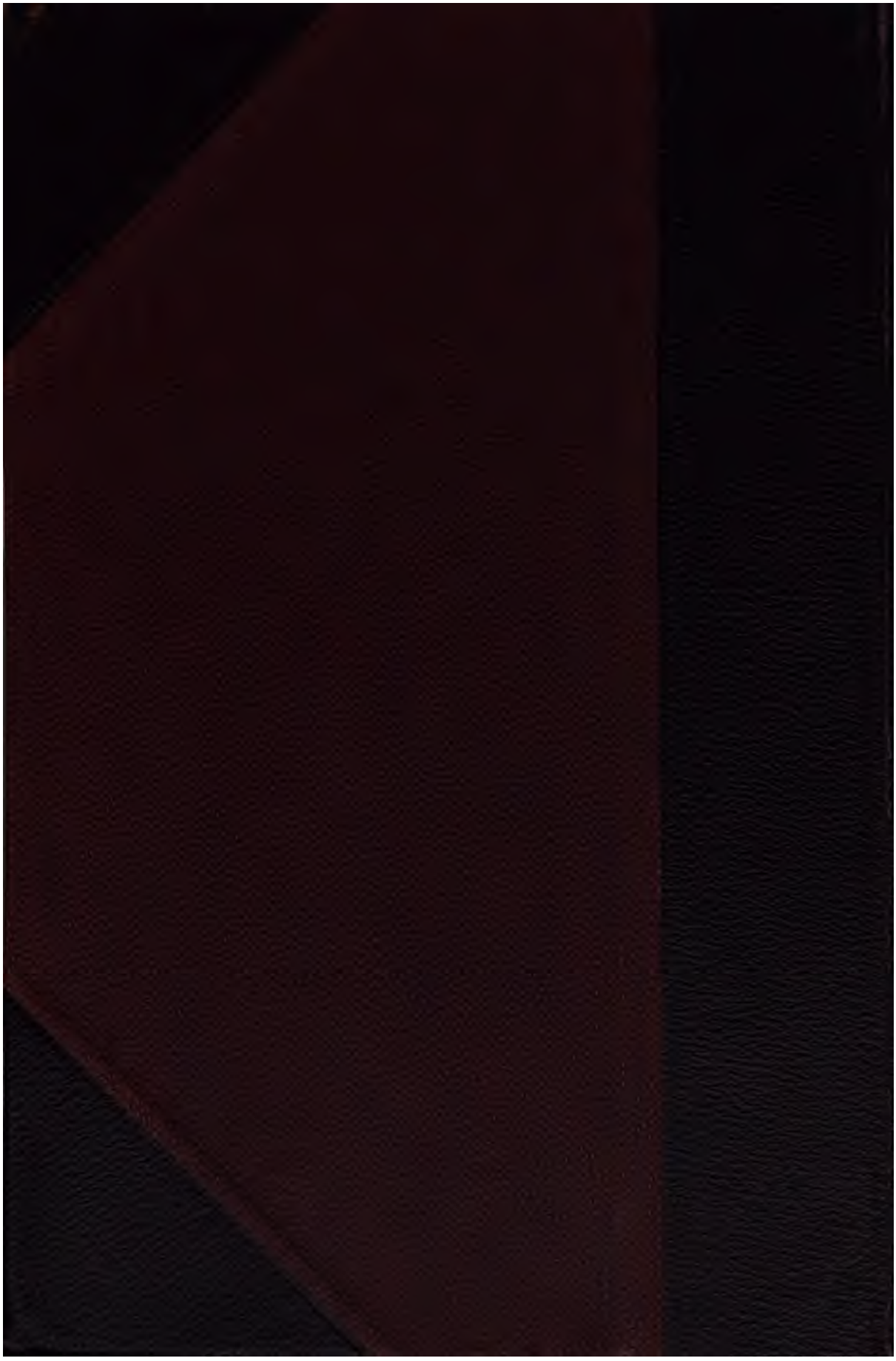
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